PB91-127803

Method for the Supercritical Fluid Extraction of Soils/Sediments

Mid-Pacific Environmental Lab., Mountain View, CA

Prepared for:

Environmental Monitoring Systems Lab., Las Vegas, NV

Nov 90

U.S. Department of Commerce
National Technical Information Service
NTIS

PB91-127803

EPA/600/4-90/026
November 1990

METHOD FOR THE SUPERCRITICAL FLUID EXTRACTION OF SOILS/SEDIMENTS

By

Viorica Lopez-Avila and N. S. Dodhiwala
Mid-Pacific Environmental Laboratory
Mountain View, California 94043

Contract Number 68-03-3511

Project Officer

Werner F. Beckert
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89109

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89193-3478

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before complet

1. REPORT NO. EPA/600/4-90/026

2.

3. PB91-127803

4. TITLE AND SUBTITLE
METHOD FOR THE SUPERCRITICAL FLUID EXTRACTION OF SOILS/SEDIMENTS

5. REPORT DATE
November 1990

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
V. Lopez-Avila and N.S. Dodhiwala

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Mid-Pacific Environmental Laboratory, Inc.
625-B Clyde Ave.
Mountain View, CA 94043

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
Contract No. 68-03-3511

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Monitoring Systems Laboratory-Las Vegas
Office of Research and Development
U.S. Environmental Protection Agency
P.O. Box 93478
Las Vegas, NV 89193-3478

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Supercritical fluid extraction has been publicized as an extraction method which has several advantages over conventional methods, and it is expected to result in substantial cost and labor savings. This study was designed to evaluate the feasibility of using supercritical fluid extraction as a sample extraction method for pollutants and matrices of concern to the EPA. Various matrices were spiked with compounds from several classes of pollutants and were extracted with supercritical carbon dioxide, with and without modifiers. Based on the results, a preliminary protocol was developed which was then tested with additional simple and complex matrices. Another important segment of this work was to study the influence of variables on recoveries. The results of this study indicate that supercritical fluid extraction with carbon dioxide, with or without modifiers, is an attractive method for the extraction of organic contaminants from environmental solid matrices. Potential advantages of the method include less solvent use and disposal, reduced manpower requirement, and increased speed and selectivity. However, more developmental work has to be done before supercritical fluid extraction becomes an easy-to-use, off-the-shelf method.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
256

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The work reported in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract 68-03-3511 by Mid-Pacific Environmental Laboratory. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

This is the final report for Work Assignment 2-21, EPA Contract 68-03-3511, conducted at Mid-Pacific Environmental Laboratory, Project No. 221. The project was directed by Dr. Viorica Lopez-Avila.

This report was written by Dr. Viorica Lopez-Avila. Technical support for the project was provided by Mr. N. S. Dodhiwala. We acknowledge the assistance of Lisa Balch, who performed all gas chromatographic/mass spectrometric analyses reported here, of Janet Benedicto who performed some of the gas chromatographic analyses, and of Karin Bauer of Midwest Research Institute, who provided input on the statistical analysis of the preliminary results from our method optimization study. We would also like to acknowledge the assistance of Ashok Shah and Carl Stadler of Suprex Corporation who helped with the design of the four-vessel-extraction setup on the Suprex SE-50 system.

ABSTRACT

The Environmental Protection Agency is interested in new and improved analytical methods that are faster, better, and cheaper than the present methods, and that, at the same time, are safe and environment-friendly. For a number of years, supercritical fluid extraction technique has been publicized as a new and promising technique for the extraction of organic compounds from solid matrices; however, applications of supercritical fluid extraction techniques to the extraction of compounds regulated by the Environmental Protection Agency from matrices of concern to the Agency have been rather limited. In late 1988, we began a study to develop a supercritical fluid extraction technique for environmental matrices such as soil, sediment, fly ash, etc. The approach taken in this study was carried out in various phases. In the first phase, we reviewed the literature published on the supercritical fluid extraction technique to assure that we would not duplicate the efforts of other researchers but would rather learn from their work. While the literature gathering and review took place, we contacted manufacturers of supercritical fluid extraction instrumentation to identify the most suitable equipment for this study. In the second phase of the study, we purchased a supercritical fluid extractor system and conducted a series of experiments to familiarize ourselves with the instrumentation and to determine the feasibility of extracting various classes of organic compounds from solid matrices. Sand was the primary matrix selected for investigation, although soils and sediments have also been tested. Upon completion of the second phase, we prepared a protocol that describes in detail how a solid sample should be extracted under supercritical conditions with carbon dioxide or carbon dioxide containing modifiers, the instrumentation requirements, etc. The third phase of the study was devoted primarily to method optimization, application of the supercritical fluid extraction technique to various environmental matrices (mostly standard reference materials certified for certain organic compounds), and instrument modification to increase sample throughput (e.g., installation of two and four extraction vessels for parallel extractions).

CONTENTS

Section Page

Notice ii
Preface iii
Abstract iv
Figures vi
Tables x

1 INTRODUCTION 1
2 CONCLUSIONS 5
3 RECOMMENDATIONS 6
4 EXPERIMENTAL 7
5 RESULTS AND DISCUSSION 18

5.1 Preliminary Work 18

5.1.1 PCBs and Organochlorine Pesticides 20
5.1.2 Organophosphorus Pesticides 20
5.1.3 Base/Neutral/Acidic Compounds 28
5.1.4 PAHs 39
5.1.5 Standard Reference Materials 39
5.1.6 Summary of the SFE Preliminary Work 88

5.2 Method Optimization 89
5.3 Multivessel Setup for Parallel SFE 116

5.3.1 Evaluation of Two-Vessel-Extraction Setup 116
5.3.2 Evaluation of Four-Vessel-Extraction Setup 116

5.4 Cost Considerations 134

REFERENCES 136

APPENDIX A -- EXTRACTION OF TRACE ORGANICS FROM SOILS AND SEDIMENTS USING SUPERCRITICAL FLUID EXTRACTION TECHNIQUES -- LITERATURE REVIEW A-1
APPENDIX B -- EXTRACTION PROCEDURE USING SUPERCRITICAL FLUIDS B-1

FIGURES

Number Page

1 Schematic representation of four-port and six-port valve connections for one-vessel-extraction setup 8

2 Schematic representation of two-vessel-extraction setup 9

3 Schematic representation of four-vessel-extraction setup 10

4 Percent recoveries of 17 organochlorine pesticides extracted from spiked sand with supercritical carbon dioxide 24

5 Percent recoveries of 25 organophosphorus pesticides extracted from spiked sand with supercritical carbon dioxide 28

6 Percent recoveries of 25 organophosphorus pesticides extracted from spiked sand with supercritical carbon dioxide with 10 percent methanol 32

7 Percent recoveries of additional 22 organophosphorus pesticides extracted from spiked sand with supercritical carbon dioxide with 10 percent methanol 33

8 GC/MS chromatogram of extract from sand sample spiked with 15 phenols 42

9 GC/MS chromatogram of sand sample extract 44

10 GC/MS chromatogram of extract of urban dust sample (NIST SRM 1649) extract -- Fraction 1 47

11 GC/MS chromatogram of extract of urban dust sample (NIST SRM 1649) spiked with PAHs -- Fraction 1 48

12 GC/MS chromatogram of extract of urban dust sample (NIST SRM 1649) spiked with PAHs -- Fraction 2 49

13 GC/MS chromatogram of coal fly ash sample (NIST SRM 1633a) extract -- Fraction 1 50

14 GC/MS chromatogram of extract of coal fly ash sample (NIST SRM 1633a) spiked with PAHs -- Fraction 1 51

15 GC/MS chromatogram of extract of coal fly ash sample (NIST SRM 1633a) spiked with PAHs -- Fraction 2 52

FIGURES (Continued)

Number Page

16 GC/MS chromatogram of coal sample (NIST SRM 1632a) extract -- Fraction 1 . 53

17 GC/MS chromatogram of extract of coal sample (NIST SRM 1632a) spiked with PAHs -- Fraction 1 54

18 GC/MS chromatogram of extract of coal sample (NIST SRM 1632a) spiked with PAHs -- Fraction 2 55

19 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 1 57

20 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 2 58

21 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 3 59

22 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 4 60

23 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 5 61

24 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 6 62

25 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 7 63

26 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 8 64

27 GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 9 65

28 GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 1 69

29 GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 2 70

30 GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 3 71

31 GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 4 72

32 GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 5 73

33 GC/MS chromatogram of HS-3 marine sediment extract 75

34 GC/MS chromatogram of NIST SRM 1941 marine sediment extract 77

35 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is cell volume (V) 101

36 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is moisture (M) 101

FIGURES (Continued)

Number Page

37 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is sample size (S) 102

38 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is volume modifier (C) 102

39 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is temperature (D) 103

40 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is time (T) 103

41 Relative changes in percent recovery across the 15 target analytes (Test 1). The variable is pressure (P) 104

42 Relative changes in percent recovery across the 15 target analytes (Test 1). The variables are identified as follows: pressure (P), temperature (D), moisture (M), cell volume (V), sample size (S), time (T), volume of modifier (C) 104

43 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is pressure (P) 106

44 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is temperature (D) 106

45 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is moisture (M) 107

46 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is glass beads (B) 107

47 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is volume of toluene (F) 108

48 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is volume of collection solvent (G) 108

49 Relative changes in percent recovery across the 15 target analytes (Test 2). The variable is static extraction time (E) 109

50 Relative changes in percent recovery across the 15 target analytes (Test 2). The variables are identified as follows: pressure (P), temperature (D), volume of toluene as modifier (F), volume of collection solvent (G), moisture (M), glass beads (B), and static extraction time (E) 109

FIGURES (Concluded)

Number **Page**

51 Percent recoveries of 18 nitroaromatics (Compounds 1 through 18) extracted from spiked sand 122

52 Percent recoveries of additional 18 nitroaromatics (Compounds 19 through 36) extracted from spiked sand 123

53 Percent recoveries of 19 haloethers extracted from spiked sand 125

TABLES

Number		Page
1	Experimental Conditions for Method Optimization (Test 1)	15
2	Experimental Conditions for Method Optimization (Test 2)	16
3	Method Optimization -- Design	17
4	Percent Recoveries of Aroclor 1232/1260 from Spiked Florisil Using Supercritical Carbon Dioxide	21
5	Percent Recoveries of Organochlorine Pesticides from Spiked Florisil Using Supercritical Carbon Dioxide	22
6	Percent Recoveries of Organochlorine Pesticides from Spiked Sand Using Supercritical Carbon Dioxide	23
7	Percent Recoveries of 17 Organochlorine Pesticides from Spiked Soil Using Supercritical Carbon Dioxide	25
8	Percent Recoveries and Percent RSDs of 41 Organochlorine Pesticides from Spiked Sand Using Supercritical Carbon Dioxide Modified with 10 Percent Methanol	26
9	Percent Recoveries of Organophosphorus Pesticides from Spiked Sand Using Supercritical Carbon Dioxide	27
10	Percent Recoveries of Organophosphorus Pesticides from Spiked Sand with Supercritical Carbon Dioxide with 10 Percent Methanol	29
11	Percent Recoveries of Base/Neutral/Acidic Compounds from Spiked Florisil Using Supercritical Carbon Dioxide	34
12	Percent Recoveries of Base/Neutral/Acidic Compounds from Spiked Florisil Using Supercritical Carbon Dioxide	35
13	Percent Recoveries of Base/Neutral/Acidic Compounds from Various Matrices with Supercritical Carbon Dioxide	36
14	Verification of Collection Efficiency Using Methylene Chloride as Collection Solvent	37

TABLES (continued)

Number		Page
15	Percent Recoveries of Base/Neutral/Acidic Compounds from Spiked Sand Using Supercritical Carbon Dioxide	39
16	Percent Recoveries of Acidic Compounds from Spiked Sand Using Supercritical Carbon Dioxide	40
17	Results of GC/MS Analysis of Sand Sample Extracted with Supercritical Carbon Dioxide	43
18	Percent Recoveries of PAHs from Spiked Sand Using Supercritical Carbon Dioxide	45
19	Percent Recoveries of PAHs from Spiked Sand and Spiked NIST Standard Reference Materials Using Supercritical Carbon Dioxide	46
20	Comparison of Recoveries Obtained by SFE with Certified Values Reported for SRS 103-100	56
21	Comparison of Recoveries Obtained by SFE with Certified Values Reported for SRS 103-100	66
22	Comparison of Recoveries Obtained by SFE with Certified Values Reported for SRM HS-3	68
23	Comparison of Recoveries Obtained by SFE with Certified Values Reported for SRM HS-3	74
24	Comparison of Recoveries Obtained by SFE with Certified Values Reported for NIST SRM 1941	76
25	Concentrations of Compounds Extracted with Supercritical Carbon Dioxide from Creosote-Contaminated Soil Samples	78
26	Concentrations of Compounds Extracted from Creosote-Contaminated Soil Samples with Supercritical Carbon Dioxide Containing 10 Percent Methanol	80
27	Concentrations of Compounds Extracted from Creosote-Contaminated Samples by Sonication with Methylene Chloride/Acetone (1:1)	82
28	Surrogate Recoveries in Fraction 1 (Supercritical Carbon Dioxide)	84
29	Surrogate Recoveries in Fraction 2 (Supercritical Carbon Dioxide)	85
30	Surrogate Recoveries in Fraction 1 (Supercritical Carbon Dioxide with 10 Percent Methanol)	86

TABLES (continued)

Number Page

31 Surrogate Recoveries in Fraction 2 (Supercritical Carbon Dioxide with 10 Percent Methanol) 87

32 Extraction of SRS 103-100 with Supercritical Carbon Dioxide Under Various Conditions (Test 1) 90

33 Extraction of SRS 103-100 with Supercritical Carbon Dioxide Under Various Conditions (Test 2) 91

34 Group Differences for Each of the Target Analytes Under Various Experimental Conditions (Test 1) 92

35 Group Differences for Each of the Target Analytes Under Various Experimental Conditions (Test 2) 93

36 Variable Ranks Based on Relative Changes (Test 1) 94

37 Data Sorted by Variable and Compound (Test 1) 95

38 Data Sorted by Absolute Percent Change by Compound (Test 1) 98

39 Variable Ranks Based on Relative Changes (Test 2) 105

40 Data Sorted by Variable and Compound (Test 2) 110

41 Data Sorted by Absolute Percent Change by Compound (Test 2) 113

42 Method Optimization -- Percent Recoveries 117

43 Significance Levels from ANOVA 120

44 Percent Recoveries of Nitroaromatics from Spiked Sand 121

45 Percent Recoveries of Haloethers from Spiked Sand 124

46 Average Recoveries and Percent RSDs for 19 Haloethers Extracted from Spiked Sand 126

47 Average Recoveries and Percent RSDs for 42 Organochlorine Pesticides from Spiked Sand 127

48 Average Recoveries and Percent RSDs for 46 Organophosphorus Pesticides from Spiked Sand 128

49 Average Recoveries and Percent RSDs for 30 Target Analytes Spiked on Different Matrices 131

TABLES (concluded)

Number Page

50 Average Recoveries and Percent RSDs for 15 Target Analytes Extracted from SRS 103-100 with Supercritical Carbon Dioxide (Fraction 1) 133

51 Cost Considerations -- SFE Versus Conventional Soxhlet Extraction 135

SECTION 1

INTRODUCTION

The Environmental Protection Agency (EPA) is interested in new and improved analytical methods that are faster, better, and cheaper than present methods, and that, at the same time, are safe and environmental-friendly (by minimizing the generation of waste). Such methods, when not developed specifically for the analysis of environmental samples, must be adapted to EPA needs with respect to matrices, analytes or analyte groups, sample sizes, data quality objectives (precision and accuracy requirements), etc. The methods should be generic, as far as analytes and matrices are concerned, and they should not be restricted to any particular brand of instrumentation or equipment.

An important step in the analysis sequence for organic pollutants is extraction of analytes from the samples, that means, their separation from the matrices. The sample extraction technique should, to the extent possible, yield quantitative recoveries of the target analytes from the matrices, be selective so that extraction of interferants is minimized, not generate large volumes of waste solvents, require little sample and extract handling to minimize analyte losses and contamination, and be fast and inexpensive. For the extraction of organic pollutants from solid samples (soil, sediment, tissue, fly ash, etc.), two methods are at present included in the SW-846 methods manual (1): Soxhlet extraction (Method 3540) and sonication extraction (Method 3550). A third extraction method has been developed, Soxtec extraction (which is basically a modification of Soxhlet extraction), and the required equipment is available. These three methods are being evaluated for their relative merits by the Mid-Pacific Environmental Laboratory, under contract to the EPA-Las Vegas.

For a number of years, a new and promising technique for the extraction of organic compounds from solid matrices has been publicized: supercritical fluid extraction (SFE). This method is already being used in certain industrial processes, e.g., extraction of caffeine from coffee, tea, and cocoa, and additional applications are being considered. Hundreds of patents have been granted; McHugh and Krukonis discuss in their 1986 book (2) 95 selected patents.

The actual, or claimed, advantages of SFE over conventional extraction methods include:

- SFE is much faster than Soxhlet extraction; extraction times of as little as 1 min can result in quantitative recoveries.
- No toxic and expensive solvents are required which results in reduced materials and waste disposal costs, and in reduced environmental pollution. No solvent removal or glassware cleaning is required.
- SFE conditions can easily be optimized by just varying pressure and temperature and by using modified supercritical fluids (SFs).

- Overall, the use of SFE techniques in place of conventional methods results in substantial cost and labor savings.

The theoretical aspects of SFE have been sufficiently discussed in books and review articles, e.g., in Reference 2. In principle, SFE is similar to other solvent extraction techniques, except that the solvent is in its supercritical state. SFs have some unique properties: their viscosities are much lower than those of liquids and their surface tension is zero. That means that they can penetrate into the pores of solids much more easily than liquids, almost like gases. Their densities are close to those of liquids which means that their capacities for carrying dissolved materials are similar to those of liquids.

As a first approximation, the solvent power of a SF can be related to the solvent density in the critical region. The density of a SF near its critical pressure p_c (but at $p > p_c$), at constant temperature (at $T > T_c$), changes drastically with small changes in pressure, and, as a consequence, so does the SF's solubilizing ability. On the other hand, when the temperature T (at $T > T_c$) is increased, at constant p ($p > p_c$), solubility can drastically decrease. Diffusivities of solutes in supercritical carbon dioxide are one to two orders of magnitude higher than those in liquids. An increase in temperature (at $T > T_c$) results in an increase in diffusivity. Again, this effect is most pronounced at p slightly above p_c. The viscosities of SFs increase with increasing pressure (at $p > p_c$), but they are still about an order of magnitude below the typical viscosities of liquid organic solvents.

The most commonly used SF is carbon dioxide; others that are being used, or have been investigated, include nitrous oxide, sulfur hexafluoride, Freon-13, ammonia, xenon, and several hydrocarbons. Carbon dioxide is so popular because of its low critical temperature (31.3°C) and pressure (72.9 atm), and because it is nontoxic, nonflammable, and its use does not result in a waste disposal problem.

Utilization of the unique extraction properties of SFs for the preparation of analytical samples has been demonstrated in a number of reports in the recent technical literature. However, applications involving extraction of compounds regulated by the Environmental Protection Agency have been quite limited. The publications summarized below are dealing specifically with such types of compounds. A more detailed discussion of the applications reported in the literature can be found in Appendix A of this report.

Brady et al. (3) investigated SFE of polychlorinated biphenyls (PCBs), DDT, and toxaphene from soils using carbon dioxide at 40°C and 100 atm. They showed that approximately 70 percent of the DDT and 75 percent of the toxaphene can be extracted in 10 min from a 10-g topsoil sample spiked with 1,000 ppm DDT and 400 ppm toxaphene by using supercritical carbon dioxide at a rate of 0.7 g/sec. The extraction of PCB-spiked subsoil resulted in recoveries higher than 90 percent in 1 min under the same conditions and at the same carbon dioxide flow rate. The organic and the water content of the soil sample were reported to be the two primary factors affecting the extraction efficiency.

Extraction of organic compounds from urban particulate matter and from sediments under supercritical conditions was investigated by Schantz and Chesler (4). Samples of 1 g urban particulate matter or 6 g sediment were extracted with supercritical carbon dioxide at 40°C and 345 atm. The SF was depressurized through a combination of capillary and packed-column restrictors, and the extracted components were deposited onto a C_{18}-bonded-phase packed column. No breakthrough was found on a second collector column placed in series with the first one. The extraction efficiencies for PCBs from sediments and for polynuclear aromatic hydrocarbons (PAHs) from urban particulate matter were compared with Soxhlet extraction efficiencies. The data showed that comparable amounts of PCBs and PAHs [except indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene] were extracted using Soxhlet and SFE techniques. The SFE, however, was faster than the Soxhlet extraction. Furthermore, the values obtained for indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene by SFE were 30 percent and 18 percent, respectively, higher than the certified values.

Smith and coworkers (5-8) used SFs (carbon dioxide, isobutane, and methanol-modified carbon dioxide) for the extraction of PAHs, 1-nitropyrene, benzanthrone, and nitrogen- and sulfur-containing PAHs from various adsorbent and particulate matrices. Two-gram quantities of urban dust or 1-g quantities of adsorbent materials (XAD-2, Spherocarb) were extracted with various SFs at pressures up to 400 bar and temperatures up to 235°C. Polar compounds such as 1-nitropyrene were extracted most efficiently with supercritical carbon dioxide containing methanol as modifier, whereas isobutane was most efficient for the higher-molecular-weight PAHs and the less polar compounds.

Hawthorne and Miller (9-12) used supercritical carbon dioxide and nitrous oxide with and without addition of modifiers to extract PAHs from 20-mg samples of urban dust and 50-mg samples of fly ash and river sediment, and reported that nitrous oxide with 5 percent methanol gave recoveries of 100 percent for fluoranthene and benzo(a)anthracene, 85 percent for benzo(a)pyrene, and slightly less than 50 percent for indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene from urban dust. The recoveries of PAHs from fly ash and river sediment with supercritical nitrous oxide with 5 percent methanol were better then those obtained with supercritical carbon dioxide with 5 percent methanol, supercritical carbon dioxide, and supercritical ethane.

Other compounds extracted from soil, sediment, and fly-ash samples with supercritical carbon dioxide include several triazine herbicides (13), and polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) (14,15). The triazine herbicides were extracted from 0.5-g spiked sediment samples with carbon dioxide at 230 bar and 48°C (13). Recoveries of propazine, terbutylazine, atrazine, and cyanazine were quantitative (82.4 to 96.4 percent); the simazine recoveries were only 42.5 percent. Addition of 20 µL methanol to the 0.5-g sediment sample increased the recovery of simazine to 92.0 percent. The PCDDs and PCDFs were extracted quantitatively from 0.8-g fly-ash samples with nitrous oxide at 400 atm and 40°C. Supercritical carbon dioxide did not extract the PCDDs, and only small amounts of PCDFs were found in the extraction mixture; however, supercritical carbon dioxide modified with 10 percent benzene was reported to extract the PCDDs and PCDFs quantitatively (14).

The solubilizing properties of supercritical carbon dioxide were reported to be comparable to those of hexane (12) and benzene (13), but polar modifiers, such as acetone or methanol, when added to carbon dioxide, improved both solvent strength and selectivity. For example, Dobbs et al. (16) reported that the addition of 3.5 mol-percent methanol to supercritical carbon dioxide increased the solubility of 2-aminobenzoic acid by 620 percent. For benzoic acid, the solubility enhancement was significantly greater with methanol than with acetone or n-octane. Dooley et al. (17) reported that supercritical carbon dioxide with 5 percent methanol is much more effective than supercritical carbon dioxide alone in extracting DDT from soil samples when the supercritical fluid at 100 atm and either 40°C or 80°C was "passed continuously through a fixed bed of 10 g soil."

The studies summarized above represented a good source of information when we first started on this project. However, many questions regarding experimental conditions (pressure, temperature, sample size, modifier, etc.), instrumentation (extraction vessel design, restrictor length, collection system, etc.), and sample matrix effects could not be answered because the first series of papers published in the literature did not address method optimization, and the results reported were obtained primarily with home-made equipment.

The study described in this report was carried out in various phases. In the first phase, we reviewed the literature published on the SFE technique to assure that we would not duplicate the efforts of other researchers but would rather learn from their work. The literature review is included as Appendix A of this report. While the literature gathering and review took place, we contacted manufacturers of SFE instrumentation to identify the most suitable equipment for this study. In the second phase, we purchased an off-line supercritical fluid extractor system from Suprex Corporation and conducted a series of experiments to familiarize ourselves with the instrumentation and to determine the feasibility of extracting various classes of organic compounds from solid matrices. Sand was the primary matrix selected for investigation, although a few soils and sediments have also been tested. Upon completion of the second phase, we prepared a protocol that describes in detail how a solid sample should be extracted by SFE, the instrumentation requirements, etc. This protocol is included as Appendix B of this report. The third phase was devoted primarily to method optimization, application of the SFE technique to various environmental matrices, and instrument modification to increase sample throughput (e.g., installation of two and four extraction vessels for parallel extractions). The fourth phase which will not be discussed in this report will address the evaluation of various SFE systems that are available commercially.

Subsequent sections of this report present the conclusions and recommendations derived from this study, details of the experimental procedures, and the results and discussion.

SECTION 2

CONCLUSIONS

The results of this study indicate that SFE with carbon dioxide or carbon dioxide containing modifiers is an attractive method for the extraction of organic contaminants from solid matrices. Carbon dioxide is nontoxic and creates no waste-disposal problems. Potential advantages of the method include reduced solvent use and manpower, speed, and selectivity (in combination with modifiers). However, more developmental work has to be done before SFE becomes an easy-to-use, off-the-shelf method.

Most of the matrices investigated in this study belong to the "easy" ones. However, because of the lack of standard reference materials with matrices and pollutants of environmental concern, it is currently impossible to determine absolute extraction efficiencies for most analytes because in most cases, removal of a spike from a sample matrix is much easier than removal of "incorporated" or "native" compounds. This, however, is a problem that hampers the evaluation of all extraction methods, not just SFE, and one is usually confined to comparing relative extraction efficiencies.

As a first step of method optimization, two sets of seven variables that were expected to have a significant effect on the SFE technique were investigated. Four of these variables were found to have a significant impact and were subsequently investigated in the second step of the method optimization.

A commercially available off-line extractor was modified to allow simultaneous extraction of up to four samples. Modifications made involved addition of a multiport manifold for the distribution of supercritical fluid to four extraction vessels and of a 12-port, two-way switching valve that allowed collection of two fractions per sample in unattended operation.

SECTION 3

RECOMMENDATIONS

The experimental work described in this report was performed mainly with carbon dioxide as SF and with carbon dioxide modified with 10 percent methanol. Although target compound recoveries indicate that carbon dioxide performs well in the case of spiked sand, the extraction efficiencies we achieved with other matrices were low and varied considerably. Some of our recoveries were much lower than those published by others. On close evaluation, it turns out that many of the studies reported so far in the literature were more of a qualitative nature, were often conducted with homemade equipment, focused mostly on PAHs, and used small sample sizes (as small as a few milligrams). Nonetheless, we should explore other supercritical fluids (e.g., sulfur hexafluoride, nitrous oxide) or carbon dioxide with other modifiers for extracting environmental matrices. This will allow us to determine to what extent some SFs are more advantageous than others in extracting certain target analytes from the matrix.

The SFE protocol included as Appendix B to this report was written primarily for a Suprex extractor system since this was the only system we had access to during the study. Other off-line extractors have been developed since our study began; therefore, these systems should be evaluated and the protocol should be modified to consider the new designs in SFE instrumentation.

SECTION 4

EXPERIMENTAL

Apparatus

- Supercritical fluid extraction system -- Suprex Model SE-50 consisting of a 250-mL syringe pump with the necessary valves and connecting lines to the extraction vessel, a control module containing a microprocessor for controlling the SFE system and able to store up to 25 extraction programs, an oven module consisting of the extraction oven, the extraction vessel, a 4-port and a 6-port valve configured with electronic actuators for automated operation. The system was set up either with one, two, or four extraction vessels for parallel extractions (Figures 1 to 3). Single extractions were performed with 7.8-, 4.7- or 2.0-mL vessels, parallel extractions were performed only with 2.0-mL vessels. The 7.8-mL extraction vessel (1 cm ID x 10 cm length) and the 4.7-mL extraction vessel (1 cm ID x 6 cm length) were obtained from YMC Inc. (Morris Plains, New Jersey); the 2-mL extraction vessels (0.9 cm ID x 3 cm length) were obtained from Alltech Associates (Deerfield, Illinois). Supercritical pressures were maintained inside the extraction vessels by using 60 cm of uncoated fused-silica tubing (50 μm ID x 375 μm OD) from J&W Scientific as restrictor. Collection of the extracted material was performed by inserting the outlet restrictor into a 15-mm x 60-mm glass vial (Supelco Inc., Bellefonte, Pennsylvania) containing an organic solvent spiked with a known concentration of an internal standard (terphenyl-d_{14}).

  Hexane was used as collection medium for the experiments performed with carbon dioxide, and methylene chloride or methanol was used as collection medium for the experiments performed with carbon dioxide modified with 10 percent methanol.

  To convert to a four-extraction vessel setup, we added an eight-port manifold and a 12-port, two-position switching valve (Suprex Catalog No. 223-30000-05). Figure 3 shows a schematic diagram of the four-vessel-extraction setup. Eight restrictors were mounted in the 12-port valve to allow collection of two fractions per sample. Fractions 1A, 2A, 3A, and 4A were collected when the 12-port valve was in the load position. Fractions 1B, 2B, 3B, and 4B were collected when the 12-port valve was in the inject position.

- Gas chromatograph -- A Varian 6000 equipped with two constant- current/pulsed-frequency electron capture detectors and two megabore fused-silica open-tubular columns (30-m x 0.53-mm ID DB-5 column and 30-m x 0.53-mm ID DB-1701 column), connected to a press-fit Y-shaped glass splitter (J&W Scientific Inc., Folsom, California) was used to analyze for organochlorine pesticides. The

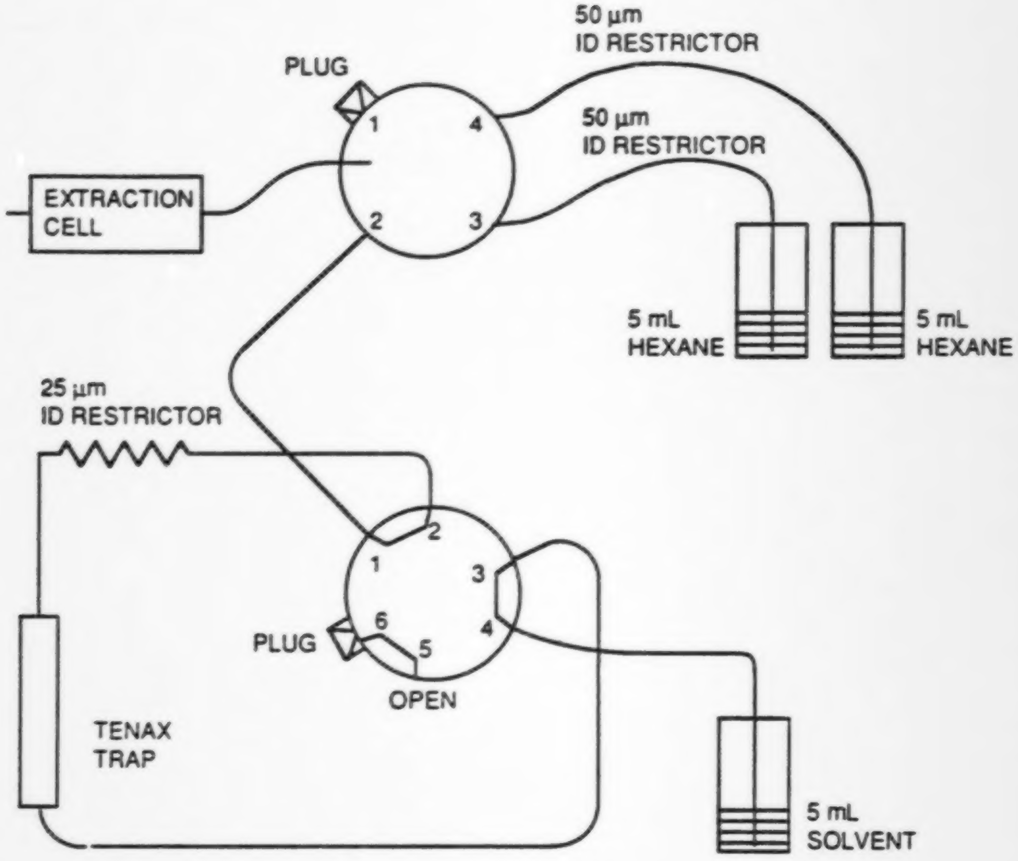
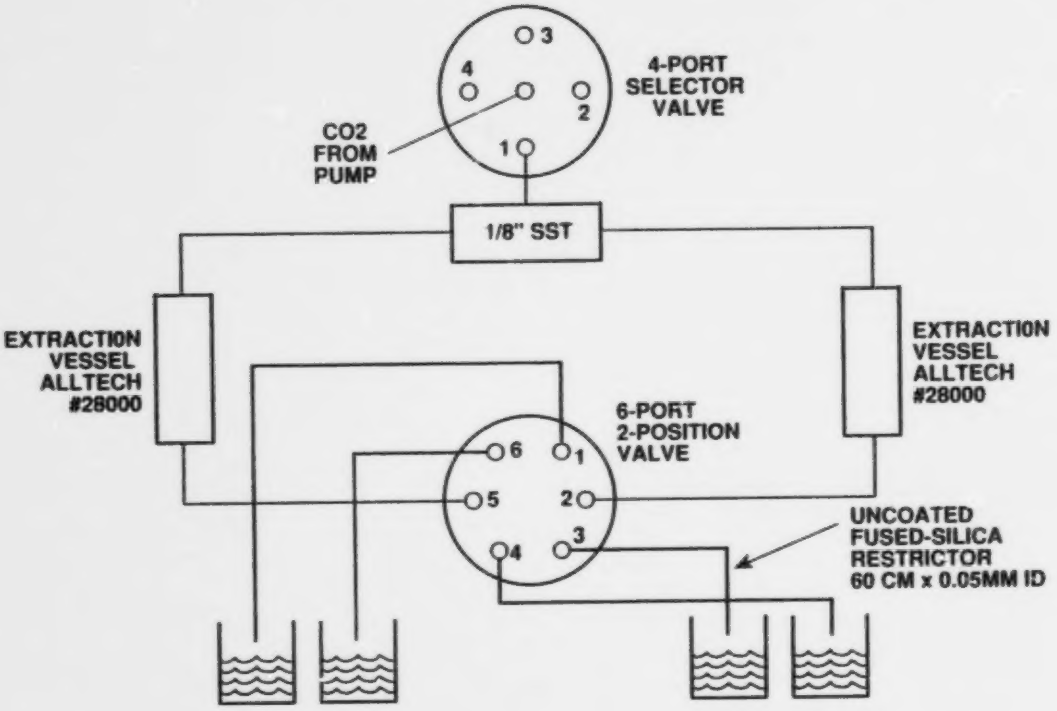
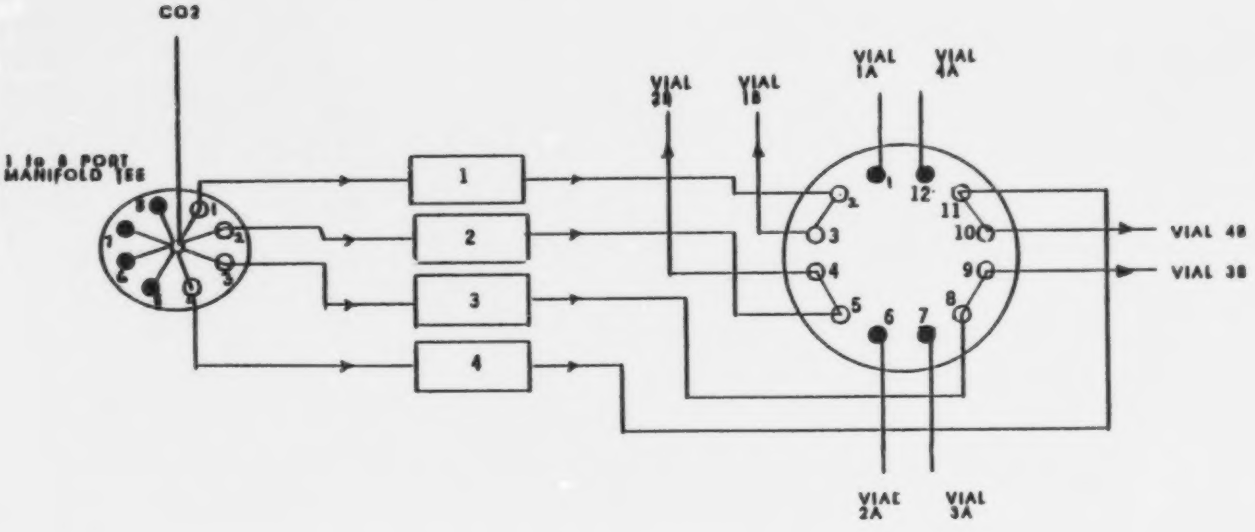

50 µm
ID RESTRICTOR
PLUG
1
4
50 µm
ID RESTRICTOR
EXTRACTION
CELL
2
3
5 mL
HEXANE
5 mL
HEXANE
25 µm
ID RESTRICTOR
2
1
3
6
4
PLUG
5
OPEN
TENAX
TRAP
5 mL
SOLVENT

Figure 1. **Schematic representation of four-port and six-port valve connections for one-vessel-extraction setup.**

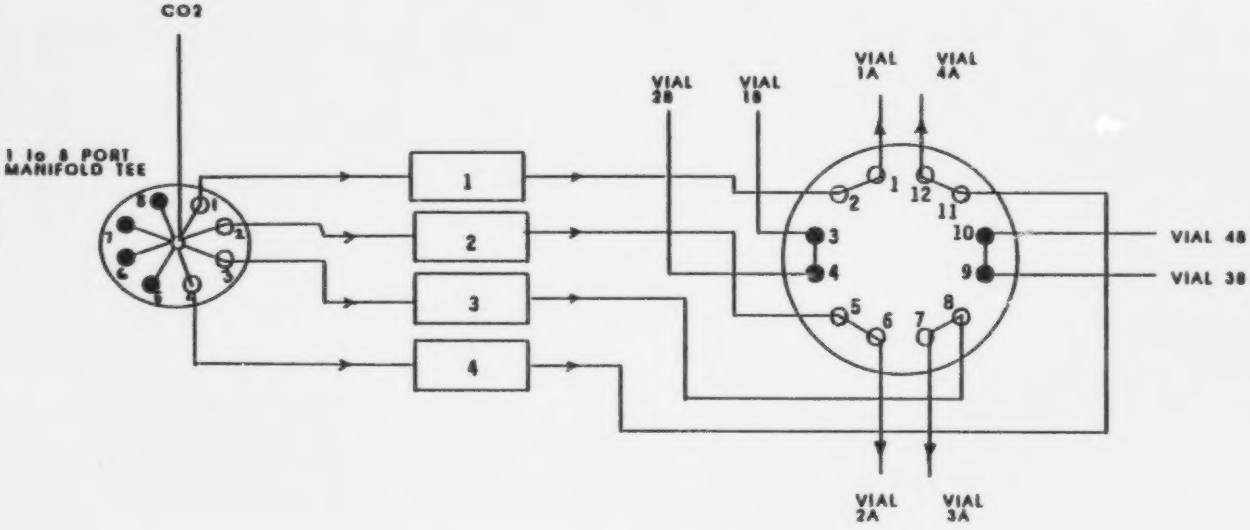


3
4
2
1
4-PORT
SELECTOR
VALVE
CO2
FROM
PUMP
1/8" SST
EXTRACTION
VESSEL
ALLTECH
#28000
EXTRACTION
VESSEL
ALLTECH
#28000
6-PORT
2-POSITION
VALVE
6
1
5
2
4
3
UNCOATED
FUSED-SILICA
RESTRICTOR
60 CM x 0.05MM ID

Figure 2. Schematic representation of two-vessel-extraction setup.


CO2
1 to 8 PORT MANIFOLD TEE
1
2
3
4
VIAL 2B
VIAL 1B
VIAL 1A
VIAL 4A
VIAL 4B
VIAL 3B
VIAL 2A
VIAL 3A

Inject Position


CO2
1 to 8 PORT MANIFOLD TEE
1
2
3
4
VIAL 2B
VIAL 1B
VIAL 1A
VIAL 4A
VIAL 4B
VIAL 3B
VIAL 2A
VIAL 3A

Load Position

Figure 3. Schematic representation of four-vessel-extraction setup.

columns were temperature programmed from 150°C (0.5-min hold) to 190°C (2-min hold) at 12°C/min. then to 275°C (10-min hold) at 4°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

- Gas chromatograph -- A Varian 3700 equipped with two thermionic selective detectors and two megabore fused-silica open-tubular columns (30-m x 0.53-mm ID DB-5 and 30-m x 0.53-mm ID DB-210 column) connected to a press-fit Y-shaped glass splitter (J&W Scientific Inc., Folsom, California) was used to analyze for organophosphorus pesticides. The columns were temperature programmed from 130°C (3-min hold) to 270°C (10-min hold) at 5°C/min; injector temperature 250°C; detector temperature 300°C; helium carrier gas 6 mL/min; helium makeup gas 20 mL/min.

- Gas chromatograph -- A Varian 6000 equipped with two constant-current/pulsed-frequency electron capture detectors, a 30-m x 0.53-mm ID DB-5 fused-silica open-tubular column (1.5-μm film thickness), and a 30-m x 0.53-mm ID DB-1701 fused-silica open-tubular column (1.0-μm film thickness), both connected to a press-fit Y-shaped fused-silica splitter (Restek Corporation, Bellefonte, Pennsylvania) was used to analyze for nitroaromatic compounds. The columns were temperature programmed from 120°C (1-min hold) to 200°C (1-min hold) at 3°C/min, then to 250°C (4-min hold) at 8°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

- Gas chromatograph -- A Varian 6500 equipped with two constant- current/pulsed-frequency electron capture detectors, a 30-m x 0.53-mm ID DB-5 fused-silica open-tubular column (0.83-μm film thickness), and a 30-m x 0.53-mm ID DB-210 fused-silica open-tubular column (1.0-μm film thickness), both connected to an 8-in injection tee (Supelco, Bellefonte, Pennsylvania) was used to analyze for haloethers. The columns were temperature programmed from 180°C (0.5-min hold) to 260°C (1-min hold) at 2°C/min; injector temperature 250°C; detector temperature 320°C; helium carrier gas 6 mL/min; nitrogen makeup gas 20 mL/min.

- Gas chromatograph/mass spectrometer -- A Finnigan 4510B (Finnigan MAT, San Jose, California) interfaced with a data system for data acquisition and processing and equipped with a 30-m x 0.32-mm ID DB-5 fused-silica open-tubular column (1-μm film thickness) was used for all PAH and base/neutral/acidic compound analyses. The column was temperature programmed from 40°C (4-min hold) to 300°C (6-min hold) at 8°C/min; injector temperature 270°C; interface temperature 270°C.

Materials

- Standards -- Analytical reference standards of the PAHs, PCBs and organochlorine pesticides, organophosphorus pesticides, nitroaromatics, haloethers, and base/neutral/acidic compounds were obtained from the U.S. Environmental Protection Agency, Pesticides and Industrial Chemicals Repository (Research Triangle Park, North Carolina); Aldrich Chemical (Milwaukee, Wisconsin);

UltraScientific Inc. (Hope, Rhode Island); and Chem Service (West Chester, Pennsylvania). All compounds, except the PAHs and the base/neutral/acidic compounds, were obtained as neat materials. Their purities were stated to be greater than 98 percent. Stock solutions of each test compound were prepared in pesticide-grade hexane at 1 mg/mL. Working calibration standards were prepared by serial dilution of a composite stock solution prepared from the individual stock solutions. The PAHs and the base/neutral acidic compounds were obtained as composite mixtures in methylene chloride or methylene chloride/toluene.

- Carbon dioxide and carbon dioxide modified with 10 percent methanol, SFC-grade liquids (Scott Specialty Gases, Plumsteadville, Pennsylvania)

- Sample matrices -- Sand, National Institute of Standards and Technology (NIST, Gaithersburg, Maryland) SRMs 1649, 1632a, 1633a, and 1941, marine sediments HS-3, HS-4, and HS-5 (National Research Council of Canada, Halifax, Nova Scotia, Canada), PAH-contaminated soil SRS 103-100 (Fisher Scientific, Pittsburgh, Pennsylvania), three soil samples received from EPA-Las Vegas identified as Samples D69Z3Z, YJU963, and H59VW5, a soil sample certified by Environmental Resource Associates (Arvada, Colorado) and ten creosote-contaminated soils received from EPA-Las Vegas. The NIST SRM 1649 is an urban dust sample collected in the Washington, D.C. area using a baghouse. The material was collected over a period of 12 months and was certified for five PAHs. The NIST SRMs 1632a and 1633a are coal and coal fly ash, respectively. The NIST SRM 1941 is a marine sediment collected from the Chesapeake Bay. The sediment was air dried, pulverized, sieved (< 150 μm sieve), homogenized in a cone blender, and subsampled (~70 g) into amber glass bottles with Teflon-lined screw caps. The bottled samples were radiation (^{60}Co) sterilized. The material was certified for 11 PAHs. The HS-3, HS-4, and HS-5 sediments were collected from a harbour in Nova Scotia; the material was freeze dried, sieved to pass a 125-μm sieve, homogenized in a modified cement mixer, then subsampled into solvent-rinsed pint-sized steel cans. The material was certified for 16 PAHs. The SRS 103-100 PAH-contaminated soil was certified for 13 PAHs, dibenzofuran, and pentachlorophenol. The Environmental Resource Associates soil was certified for nine base/neutrals, six acids, and four organochlorine pesticides. No information could be obtained about the preparation of the SRS 103-100, the EPA-Las Vegas materials, or the Environmental Resource Associates soil.

Sample Extraction for Evaluation of One-Vessel-Extraction Setup

The extraction of 17 organochlorine pesticides from the three soil samples was performed at 150 atm and 50°C (10 min static)/200 atm and 60°C (10 min dynamic)/250 atm and 70°C (10 min dynamic) using carbon dioxide only. Sample size was 8 g for sample D69Z3Z and 5 g for samples YJU963 and H59VW5.

The extraction of 41 organochlorine pesticides from sand (8 g) spiked at 62.5 ng/g (except for a few compounds at higher concentrations) was performed at 150 atm and 50°C (10 min static)/200 atm and 60°C (10 min dynamic)/250 atm and 70°C (10 min dynamic) using carbon dioxide modified with 10 percent methanol.

The extractions of 25 organophosphorus pesticides from sand (8 g) spiked at 2.5 µg/g were performed with carbon dioxide at 200 atm and 60°C or 250 atm and 70°C with extraction times ranging from 45 to 60 min. Shorter extraction times were used for carbon dioxide modified with 10 percent methanol. In addition, a set of programmed extractions was performed with carbon dioxide/methanol at 150 atm and 50°C (10 min static)/200 atm and 60°C (10 min dynamic)/250 atm and 70°C (10 min dynamic).

The extraction of the SRS 103-100 samples was performed with carbon dioxide modified with 10 percent methanol as described below. To collect Fraction 1, the extraction was started at 150 atm and 50°C. After pressurizing the extraction vessel for 10 min, the pressure was increased to 200 atm and the temperature to 60°C. After 10 min, the pressure was increased to 250 atm and the temperature to 70°C and maintained for another 10 min. Fraction 2 was collected at 250 atm and 70°C (30 min), Fraction 3 at 300 atm and 70°C (30 min), and Fractions 4 through 9 at 350 atm and 70°C, every 30 min. No compounds were detected in Fractions 5 through 9; we therefore concluded that after Fraction 4 the extraction was complete under those conditions.

The HS-3 sample was extracted with methanol-modified supercritical carbon dioxide using the same conditions as described above for the SRS 103-100, except that only five fractions were collected from a 6-g sample; another sample (2.3 g) was extracted in duplicate, on another Suprex SE-50 system, with supercritical carbon dioxide only at 400 atm and 70°C for 25 min.

Sample Extraction for Evaluation of Two-Vessel-Extraction Setup

The extraction of 36 nitroaromatic compounds from sand spiked at 600 ng/g (per analyte) was performed at 150 atm and 50°C (10 min dynamic)/200 atm and 60°C (10 min dynamic)/250 atm and 70°C (10 min dynamic) using carbon dioxide only. Sample size was 2.5 g. Two spiked samples identified as Experiments 1 and 2 were extracted in parallel using the same conditions. Two additional sand samples spiked at the same concentrations were extracted in parallel at 300 atm and 70°C for 30 min dynamic and were identified as Experiments 3 and 4. To verify the completeness of the SFE technique, we collected an additional fraction for Experiments 1 and 2 at 300 atm and 70°C (30 min dynamic).

The extraction of 19 haloethers from sand spiked at 600 ng/g (per analyte) was performed at 250 atm and 70°C (60 min dynamic) using carbon dioxide only (Experiments 3 through 8). In Experiments 3 and 4, two sand samples (spiked in an aluminum cup with 150 µL of 10 ng/µL spiking solution) were extracted in parallel. In Experiments 5 and 6, two other sand samples (spiked directly in the extraction vessel to avoid losses due to compound volatilization and sample transfer) were extracted in parallel. In Experiments 7 and 8, two soil samples (spiked in an aluminum cup as in Experiments 3 and 4) were extracted in parallel at 150 atm and 50°C for 60 min.

Sample Extraction for Evaluation of Four-Vessel-Extraction Setup

The extraction of 19 haloethers from four spiked sand samples (2.5 g each, spiked at 600 ng/g per compound) was performed at 250 atm/60°C/60 min using carbon dioxide.

The extraction of 42 organochlorine pesticides from the four spiked sand samples (3 g each) was begun at 150 atm/50°C/10 min static, continued at 200 atm/60°C/10 min dynamic, and finished at 250 atm/70°C/10 min dynamic using carbon dioxide.

The extraction of 46 organophosphorus pesticides from spiked sand samples (2.5 g each) was performed with carbon dioxide as follows: for Trial 1, extraction was begun at 150 atm/50°C/10 min static, continued at 200 atm/70°C/10 min dynamic, and finished at 250 atm/70°C/10 min dynamic; for Trial 2, extraction was performed at 200 atm/60°C/30 min dynamic; for Trial 3, extraction was performed at 250 atm/70°C/30 min dynamic.

The extraction of the SRS 103-100 samples (2.5 g each) was performed with carbon dioxide at 300 atm/70°C/30 min. Two fractions were collected from each sample to verify the completeness of the extraction.

Method Optimization

The experimental conditions for method optimization focused on seven variables, each chosen at two levels (high and low). Two separate tests were performed to see how these variables influence the method performance. The seven variables and their values chosen for each test are presented in Tables 1 and 2. The group differences for Test 1 (V_P through V_C) were calculated using Equations 1 through 7; those for Test 2 were calculated in a similar manner.

$$V_P = 1/4(w + x + y + z) - 1/4(s + t + u + v) = p - P \tag{1}$$
$$V_D = 1/4(u + v + y + z) - 1/4(s + t + w + x) = d - D \tag{2}$$
$$V_M = 1/4(t + v + x + z) - 1/4(s + u + w + y) = m - M \tag{3}$$
$$V_V = 1/4(u + v + w + x) - 1/4(s + t + y + z) = v - V \tag{4}$$
$$V_S = 1/4(t + v + w + y) - 1/4(s + u + x + z) = s - S \tag{5}$$
$$V_T = 1/4(t + u + x + y) - 1/4(s + v + w + z) = t - T \tag{6}$$
$$V_C = 1/4(t + u + w + z) - 1/4(s + v + x + y) = c - C \tag{7}$$

Next, the relative changes as 100 x change/average recovery at low level were calculated and the data were sorted by variable and compound. The variables were ranked in increasing order of absolute relative change for each compound and the sum of ranks was calculated.

A full factorial design experiment was conducted for four variables (time, pressure, moisture, and sample size). The measurements were randomized as in Table 3. A plus sign denotes that the variable is at the high level and a minus sign that it is at the low level. The last column in Table 3 gives a notation used to describe the combinations, where the presence of the appropriate lower case letter indicates that the variable is at the high level and its absence that the variable is at the low level. All experiments were performed in duplicate with the SRS 103-100 soil. The values for the four variables were as follows: time (1 hr and 2 hrs), pressure(250 atm and 350 atm), moisture (10 percent and 25 percent), and sample size (1 g and 2.5 g). The duplicate experiments were performed in parallel by splitting off the incoming carbon dioxide to two extraction vessels. All other parameters were kept constant as follows: temperature 70°C, collection solvent -- hexane 5 mL, restrictor 50 µm ID, no static extraction, extraction vessel 2 mL.

From the recovery data that we obtained for the 32 experiments, we established the effect of the individual variables, the interaction between the two variables, and the interaction between three variables. The SAS program was used in the analysis of variance.

TABLE 1. EXPERIMENTAL CONDITIONS FOR METHOD OPTIMIZATION (TEST 1)

Code letter	Variable	Exp. 1 s	Exp. 2 t	Exp. 3 u	Exp. 4 v	Exp. 5 w	Exp. 6 x	Exp. 7 y	Exp. 8 z
P	Pressure (atm)	300	300	300	300	150	150	150	150
D	Temperature (°C)	70	70	50	50	70	70	50	50
M	Moisture (%)	10	0	10	0	10	0	10	0
V	Cell volume (mL)	4.7	4.7	2.0	2.0	2.0	2.0	4.7	4.7
S	Sample size (g)	2.5	1.0	2.5	1.0	1.0	2.5	1.0	2.5
T	Time (min)	60	30	30	60	60	30	30	60
C	Modifier volume[a] (µL)	250	50	50	250	50	250	250	50

[a] Hexane was used as modifier. This experiment was initially set up to investigate not only the extraction of polynuclear aromatic hydrocarbons, but also of a set of organochlorine pesticides, which was spiked on the standard reference material at a low and a high concentration. The low and high concentrations were obtained by spiking 50 µL and 250 µL, respectively, of a hexane solution containing the compounds. Since the organochlorine pesticides could not be detected due to high background, the parameter "analyte spike" was changed to "modifier volume".

TABLE 2. EXPERIMENTAL CONDITIONS FOR METHOD OPTIMIZATION (TEST 2)

Code letter	Variable	Exp. 1 s	Exp. 2 t	Exp. 3 u	Exp. 4 v	Exp. 5 w	Exp. 6 x	Exp. 7 y	Exp. 8 z
P	Pressure (atm)	300	300	300	300	150	150	150	150
D	Temperature (°C)	70	70	50	50	70	70	50	50
F	Volume of toluene (μL)[a]	500	0	500	0	500	0	500	0
G	Collection volume (mL)	5.0	5.0	1.0	1.0	1.0	1.0	5.0	5.0
M	Moisture (%)	10	0	10	0	0	10	0	10
B	Glass beads	y	n	n	y	n	y	y	n
E	Static extraction time (min)	30	15	15	30	15	30	30	15

[a] Toluene was used as modifier.

TABLE 3. METHOD OPTIMIZATION -- DESIGN[a]

Exp.	Time	Pressure	Moisture	Sample size	Combination
FD1	-	-	-	-	1
FD2	+	-	-	-	a
FD3	-	+	-	-	b
FD4	-	-	+	-	c
FD5	-	-	-	+	d
FD6	+	+	-	-	ab
FD7	-	+	+	-	bc
FD8	-	-	+	+	cd
FD9	+	-	+	-	ac
FD10	-	+	-	+	bd
FD11	+	-	-	+	ad
FD12	+	+	+	-	abc
FD13	+	+	-	+	abd
FD14	+	-	+	+	acd
FD15	-	+	+	+	bcd
FD16	+	+	+	+	abcd

[a] The values for the four parameters were as follows: time (1 hr and 2 hrs), pressure (250 atm and 350 atm), moisture (10 percent and 25 percent), and sample size (1 g and 2.5 g). The duplicate experiments were performed in parallel by splitting off the incoming carbon dioxide to two extraction vessels. All other parameters were kept constant as follows: temperature 70°C, collection solvent -- hexane 5 mL, restrictor 50 μm ID, no static extraction, extraction vessel 2 mL.

SECTION 5

RESULTS AND DISCUSSION

5.1 PRELIMINARY WORK

This section addresses the preliminary work performed for various classes of organic compounds including PCBs and organochlorine pesticides, organophosphorus pesticides, the base/neutral/acidic compounds targeted by EPA under the Contract Laboratory Program, and selected PAHs. The various experiments are summarized below:

- Two Aroclors (Aroclor 1232 and 1260) were spiked on Florisil at 5 µg/g; the spiked samples were then extracted with supercritical carbon dioxide at three temperatures (40, 50, and 60°C) and four pressures (120, 150, 200, and 230 atm) to establish the optimum conditions for temperature and pressure.

- Sixteen organochlorine pesticides were spiked on Florisil at 5 µg/g; the spiked samples were then extracted with supercritical carbon dioxide at 50°C and 150 or 200 atm for up to 20 min.

- Seventeen organochlorine pesticides were spiked on sand at 2.5 µg/g and on soil (dry and moist) at 16, 50, and 80 ng/g; the spiked samples were then extracted with supercritical carbon dioxide under various conditions.

- Forty-one organochlorine pesticides were spiked on sand at 62.5 to 1,875 ng/g and the spiked samples were then extracted with supercritical carbon dioxide modified with 10 percent methanol.

- Twenty-five organophosphorus pesticides were spiked on sand at 3.75 µg/g and the spiked samples were then extracted with supercritical carbon dioxide at different pressure/temperature conditions and with addition of modifier to the sample.

- Forty-seven organophosphorus pesticides were spiked on sand at 2.5 µg/g and the spiked samples were then extracted with supercritical carbon dioxide modified with 10 percent methanol at different pressure/temperature conditions.

- Forty-three base/neutral/acidic compounds were spiked on Florisil, alumina, silica, and sand at various concentrations; the spiked samples were extracted with supercritical carbon dioxide at various conditions. Acetone was used as modifier and was added to the sample prior to extraction. Fifteen acidic compounds were spiked on sand at 100 µg/g and tested separately.

- Sixteen PAHs were spiked on sand, and on three SRMs from NIST (urban dust, coal, and coal fly ash) at various concentrations. Acetone was added to the sand sample to test the effect of modifier upon extraction efficiency. Two fractions were collected from the NIST SRM to verify the completeness of the SFE technique.

- Three SRMs (SRS 103-100 certified for 13 PAHs, dibenzofuran, and pentachlorophenol; HS-3 marine sediment certified for 16 PAHs; NIST SRM 1941 certified for 11 PAHs), and 10 soil samples contaminated with creosote received from EPA-Las Vegas were extracted with supercritical carbon dioxide and supercritical carbon dioxide modified with 10 percent methanol. Up to nine fractions were collected from one of the samples over a period of 270 min, however only four fractions showed detectable levels of compounds chromatographable by gas chromatography.

The results of these experiments are summarized in Subsections 5.1.1 through 5.1.5. A few observations made during the preliminary work are summarized below:

- Initially, we used a 7.85-mL extraction vessel. The amount of sample loaded to the extraction vessel was 4 g for Florisil, 8 to 11.2 g for sand, and 5 to 6 g for the samples received from EPA-Las Vegas. Smaller amounts (1 to 2 g) were used for the NIST SRMs. In this case, the void volume was filled with silanized glass wool. This extraction vessel was used continuously for a period of four months after which it developed leaks and could no longer be used. Other extraction vessels were tested (a 0.785-mL and a 1.57-mL vessel, both from Suprex Corporation, and a 0.5 mL Brownlee guard column), however, they developed leaks after the third or fourth extraction or were too difficult to work with because of their small sizes.

- Our SFE instrument was equipped by the manufacturer with a 50-cm x 25-μm ID uncoated fused-silica capillary restrictor. After a series of trial-and-error experiments with the 25-μm ID restrictor, we concluded that in order to achieve reasonable extraction efficiencies in less than 60 min, we needed a larger diameter restrictor. A 50-μm and a 100-μm ID uncoated fused-silica capillary restrictor were then tested. The flow rate through the 100-μm ID restrictor was too high for our collection device to handle; therefore, the 100-μm ID restrictor was no longer evaluated. A thick-wall (375-μm OD) 50-μm ID restrictor from J&W Scientific performed adequately. Some of the data presented in Section 5.1 were obtained with the 25-μm ID fused-silica restrictor and are identified appropriately. The rest of the data in this report were obtained with a 50-μm ID fused-silica restrictor. We have found it very useful to have the instrument set up with at least two restrictors. The restrictors were used to collect different fractions during extraction, in unattended operation. With our four-port valve setup we could collect up to four fractions per sample.

- Collection of the material extracted with supercritical carbon dioxide was done by inserting the outlet restrictor into a 15-mm x 60-mm glass vial containing 5 mL hexane spiked with a known amount of an internal standard. Terphenyl-d_{14} was used for the PAHs and the base/neutral/acidic compounds. No internal standard was used for the other groups of target compounds. Recoveries of the internal standard were better than 95 percent when the volume of the solvent was adjusted to 5 mL. During extraction, approximately 60 percent of the hexane is lost by volatilization. When working with carbon dioxide modified with 10 percent methanol, the collection solvent was either methanol or methylene chloride, and the loss of solvent during depressurization of the carbon dioxide/10 percent methanol mixture was minimal since methanol was being released continuously during extraction.

5.1.1 PCBs and Organochlorine Pesticides

Tables 4 and 5 show the recoveries of Aroclor 1232/1260 and of 16 organochlorine pesticides spiked on Florisil, respectively. A 20-min extraction using a 25-µm ID fused-silica restrictor did not give quantitative recoveries for Aroclor under any of the conditions tested. However, a 40-min extraction appeared to give recoveries > 75 percent above 200 atm and 40°C. No tests were conducted above 60°C and 230 atm. Despite the good results for the Aroclors, the recoveries of the organochlorine pesticides spiked on Florisil were unacceptable (Table 5). By changing the 25-µm ID restrictor to a 50-µm ID restrictor, we were able to obtain excellent recoveries for the 17 organochlorine pesticides (methoxychlor had been added to the 16 compounds listed in Table 5) from sand using supercritical carbon dioxide (Table 6 and Figure 4).

The 17 organochlorine pesticides listed in Table 6 were used to investigate to what extent this type of compound can be recovered from sand (8 g), spiked at 2.5 µg/g, using supercritical carbon dioxide. Figure 4 presents the plotted recovery data for the supercritical carbon dioxide extractions using various pressure/temperature combinations (pressure ranged from 150 to 250 atm, temperature ranged from 50 to 70°C). The data show that most of the organochlorine pesticides were recovered quantitatively (recoveries > 75 percent) at pressures as low as 150 atm and temperatures of 50°C. Methoxychlor was the only compound with low recoveries which ranged from 45 and 75 percent. A small amount of modifier (acetone) added to the sample resulted only in marginal recovery increases although others reported significant increases in recoveries when acetone or methanol were added directly to the sample (11).

When the same compounds were spiked onto the three soil samples from EPA-Las Vegas (both wet and dry) at concentrations in the ppb range, the recoveries were comparable to those from sand except for Sample YJU963 (Table 7). The analyte recoveries were quite low for Sample YJU963, and we attributed this to matrix effects. However, since we could not obtain any information regarding the mineralogical composition of these soil samples, we cannot speculate whether the organic carbon content, the surface area or some other effect decreased the recoveries from that sample.

The 41 organochlorine pesticides listed in Table 8 were also spiked onto sand (8 g) at the levels shown in the table and extracted with supercritical carbon dioxide with 10 percent methanol. The average recoveries and the RSDs for three determinations are presented in Table 8. Excellent recoveries were achieved for 38 of the 41 compounds. Only the recoveries for hexachlorocyclopentadiene, chlorobenzilate, and DBCP were very low. The RSDs ranged from 2.4 to 29.2 percent and were for the most part comparable to those achieved by the Soxhlet extraction and sonication methods.

5.1.2 Organophosphorus Pesticides

The 25 organophosphorus pesticides listed in Table 9 were spiked onto sand (8 g) at 2.5 µg/g and the spiked samples were extracted with supercritical carbon dioxide or carbon dioxide modified with 10 percent methanol. The recoveries from the carbon dioxide only

TABLE 4. PERCENT RECOVERIES OF AROCLOR 1232/1260 FROM SPIKED FLORISIL USING SUPERCRITICAL CARBON DIOXIDE[a]

		Percent recovery								
		40°C[b]			50°C			60°C		
Pressure (atm)	Analysis	First extraction	Second extraction	Total	First extraction	Second extraction	Total	First extraction	Second extraction	Total
120	DB-608	15.6	25.8	41.4	11.9	12.0	23.9	8.9	51.4	60.3
	DB-1701	13.6	23.9	37.5	9.6	12.2	21.8	7.7	50.4	58.1
150	DB-608	43.1	34.0	77.1	31.3	36.3	67.6	45.3	63.0	108.3
	DB-1701	41.5	32.3	73.8	29.9	35.5	65.4	44.0	59.8	103.8
200	DB-608	51.5	30.0	81.5	53.3	29.2	82.5	45.4	48.0	93.4
	DB-1701	48.1	27.1	75.2	50.9	27.6	78.5	47.1	50.6	97.7
230	DB-608	70.6	32.5	103.1	74.7	19.1	93.8	48.2	58.2	106.4
	DB-1701	63.5	28.0	91.5	72.7	17.6	90.3	47.5	56.4	103.9

[a] Spiking level of Aroclor 1232/1260 was 5 μg/g Florisil. The first extraction was performed for 20 min at the temperature and pressure indicated; the extracted Aroclors were collected in 5 mL hexane at room temperature. The second extraction was also performed for 20 min at the temperature and pressure indicated. The extraction was performed with a 7.85-mL vessel and a 50-cm x 25-μm uncoated fused-silica restrictor. Sample size was 4 g.

[b] The temperature varied slightly from 40°C to 42°C.

TABLE 5. PERCENT RECOVERIES OF ORGANOCHLORINE PESTICIDES FROM SPIKED FLORISIL USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	150 atm/50°C 20 min dynamic	150 atm/50°C 10 min static 10 min dynamic	200 atm/50°C 10 min static 10 min dynamic	200 atm/50°C 20 min dynamic
1	alpha-BHC	37.0	21.9	16.5	37.3
2	gamma-BHC	29.7	27.2	13.1	28.4
3	beta-BHC	17.2	17.1	8.1	21.0
4	Heptachlor	34.3	14.8	15.9	40.0
5	delta-BHC	16.5	22.2	7.0	13.6
6	Aldrin	19.6	8.2	10.8	31.2
7	Heptachlor epoxide	17.2	26.3	7.1	16.0
8	Endosulfan I	13.9	21.2	4.8	11.2
9	4,4 -DDE	37.2	18.0	17.7	41.1
10	Dieldrin	9.4	14.6	3.0	6.2
11	Endrin	6.4	12.1	2.0	4.4
12	4,4 -DDD	20.9	24.2	9.7	23.1
13	Endosulfan II	3.3	5.6	1.1	2.2
14	4,4 -DDT	22.8	23.2	11.2	26.9
15	Endrin aldehyde	2.4	3.6	0.8	1.7
16	Endosulfan sulfate	2.3	5.3	1.0	2.4

[a] All experiments were performed with a 7.85-mL extraction cell. 4 g Florisil was used for each experiment. Spiking level of the organochlorine pesticides was 20 μg per 4 g Florisil (100 μL of a methanolic solution at 0.2 μg/μL was spiked in each case). A 25-μm x 50-cm length uncoated fused-silica restrictor (Suprex Corporation) was used.

TABLE 6. PERCENT RECOVERIES OF ORGANOCHLORINE PESTICIDES FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Exp. 1[b]	Exp. 2[c]	Exp. 3[d]	Exp. 4[e]
1	alpha-BHC	102.6	95.9	102.8	101.0
2	gamma-BHC	97.1	96.8	101.9	98.7
3	beta-BHC	93.9	92.4	100.5	95.2
4	Heptachlor	98.4	95.7	101.0	98.7
5	delta-BHC	92.4	95.3	101.4	97.9
6	Aldrin	81.6	82.0	90.4	86.4
7	Heptachlor epoxide	96.9	98.6	103.0	100.8
8	Endosulfan I	95.4	96.7	102.8	98.7
9	4,4'-DDE	98.5	97.0	102.3	99.0
10	Dieldrin	96.3	98.5	103.4	99.1
11	Endrin	100.2	107.0	114.9	108.8
12	4,4'-DDD	94.8	95.9	101.9	96.6
13	Endosulfan II	81.9	97.0	96.2	89.3
14	4,4'-DDT	89.8	93.2	100.9	95.8
15	Endrin aldehyde	73.5	76.5	85.8	78.6
16	Endosulfan sulfate	62.4	72.3	86.9	75.1
17	Methoxychlor	45.4	58.1	70.7	75.1

[a] All experiments were performed with a 7.85-mL extraction vessel. The amount of sand extracted was 8 g. The spiking level was 2.5 μg/g per compound. The extraction conditions are specified in footnotes b through e. A 50-μm ID x 60-cm length uncoated fused-silica restrictor (J&W Scientific) was used.

[b] Exp. 1: 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/10 min dynamic.

[c] Exp. 2: 200 atm/60°C/30 min dynamic.

[d] Exp. 3: 200 atm/60°C/30 min dynamic with 200 μL acetone modifier.

[e] Exp. 4: 150 atm/50°C/30 min dynamic.

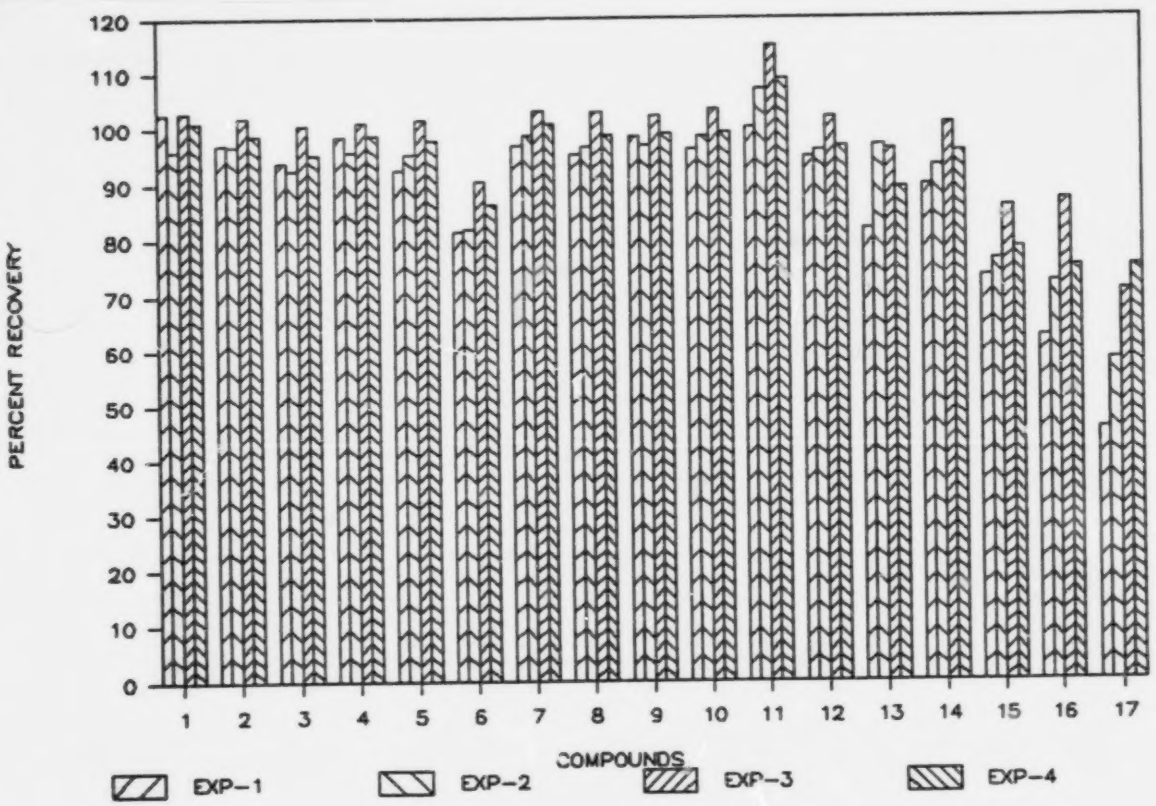


Figure 4. Percent recoveries of 17 organochlorine pesticides extracted from spiked sand (8 g) with supercritical carbon dioxide. The experiments were performed using a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1: 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2: 200 atm/60°C/30 min dynamic; Exp. 3: 200 atm/60°C/30 min dynamic with 200 μL acetone modifier; Exp. 4: 150 atm/50°C/30 min dynamic.

TABLE 7. PERCENT RECOVERIES OF 17 ORGANOCHLORINE PESTICIDES FROM SPIKED SOIL USING SUPERCRITICAL CARBON DIOXIDE

		Soil with 10 percent moisture		Dry soil	
		Sample D69Z3Z spiked at			
Compound no.	Compound	16 ng/g[a]	80 ng/g[a]	Sample YJU963[b]	Sample H59VW5[b]
1	alpha-BHC	84.0	88.1	72.9	64.7
2	gamma-BHC	91.2	94.1	70.4	66.8
3	beta-BHC	95.0	91.6	60.7	69.8
4	Heptachlor	90.2	94.7	73.3	48.4
5	delta-BHC	77.3	85.9	51.6	74.8
6	Aldrin	84.3	90.8	59.5	44.7
7	Heptachlor epoxide	93.9	97.9	66.2	55.9
8	Endosulfan I	83.0	97.7	55.9	73.6
9	4,4'-DDE	77.4	92.0	62.3	79.9
10	Dieldrin	72.4	87.1	41.6	83.5
11	Endrin	80.2	93.4	51.3	101
12	4,4'-DDD	54.5	77.1	35.9	88.3
13	Endosulfan II	76.5	91.4	22.9	76.5
14	4,4'-DDT	104	97.1	66.0	63.3
15	Endrin aldehyde	49.6	78.6	9.9	63.9
16	Endosulfan sulfate	64.5	84.8	9.5	87.3
17	Methoxychlor	68.0	85.4	c	c

[a] The sample size was 5 g.
[b] The spiking level was 50 ng/g. The sample size was 8 g.
[c] Data not available.

TABLE 8. PERCENT RECOVERIES AND PERCENT RSDs OF 41 ORGANOCHLORINE PESTICIDES FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE MODIFIED WITH 10 PERCENT METHANOL[a]

Compound no.	Compound	Spike level (ng/g)	Percent average recovery	Percent RSD
1	alpha-BHC	62.5	93.6	16.8
2	gamma-BHC	62.5	121	10.8
3	beta-BHC	62.5	93.6	25.2
4	Heptachlor	62.5	91.7	23.0
5	delta-BHC	62.5	103	19.9
6	Aldrin	62.5	98.7	15.9
7	Heptachlor epoxide	62.5	88.6	12.2
8	Endosulfan I	62.5	88.2	10.3
9	4,4'-DDE	62.5	95.4	10.6
10	Dieldrin	62.5	103	19.6
11	Endrin	62.5	92.8	13.6
12	4,4'-DDD	125	120	10.1
13	Endosulfan II	62.5	89.6	6.9
14	4,4'-DDT	62.5	99.9	4.9
15	Endrin aldehyde	125	120	10.8
16	Endosulfan sulfate	62.5	125	8.8
17	Methoxychlor	62.5	107	2.4
18	Endrin ketone	62.5	98.1	6.7
19	Hexachlorocyclopentadiene	62.5	26.1	13.7
20	Etridiazole	62.5	87.9	14.5
21	Chloroneb	1,250	92.5	20.8
22	Propachlor	1,250	95.8	22.1
23	Hexachlorobenzene	62.5	114	7.3
24	Trifluralin	125	94.5	19.7
25	Diallate	1,875	109	9.9
26	Pentachloronitrobenzene	62.5	97.8	14.8
27	Chlorothalonil	125	93.4	9.9
28	Alachlor	625	103	20.5
29	DCPA	62.5	107	5.9
30	Isodrin	62.5	98.6	17.9
31	trans-Permethrin	625	102	17.9
32	gamma-Chlordane	62.5	95.8	18.5
33	alpha-Chlordane	62.5	99.8	11.4
34	trans-Nonachlor	62.5	108	11.4
35	Captan	125	95.0	6.5
36	Perthane	1,875	79.0	8.9
37	Chlorobenzilate	125	28.4	12.6
38	Chloropropylate	62.5	109	10.3
39	Kepone	62.5	106	19.5
40	Mirex	125	96.4	3.7
41	DBCP	62.5	35.4	29.2

[a] The number of determinations was three. The sample size was 8 g. Each extraction was performed with carbon dioxide modified with 10 percent methanol at 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/ 10 min dynamic.

TABLE 9. PERCENT RECOVERIES OF ORGANOPHOSPHORUS PESTICIDES FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Exp. 1[b]	Exp. 2[b]	Exp. 3[c]
1	Dichlorvos	54.0	61.3	56.3
2	Mevinphos	0	14.7	9.7
3	Ethoprop	66.3	60.0	50.3
4	Naled	28.7	30.7	18.7
5	Sulfotep	60.0	81.3	79.3
6	Phorate	60.7	80.7	78.0
7	Dimethoate	0	0	0
8	Diazinon	0	0	0
9	Disulfoton	59.0	81.3	84.3
10	Methylparathion	57.7	74.3	70.7
11	Ronnel	59.3	80.7	85.3
12	Malathion	58.3	70.7	61.0
13	Fenthion	53.7	80.7	84.0
14	Chlorpyrifos	58.7	85.0	87.7
15	Parathion	61.0	79.7	79.7
16	Stirofos	67.3	61.0	47.0
17	Fensulfothion	0	0	0
18	Bolstar	66.3	82.0	84.7
19	EPN	66.0	78.3	76.3
20	Azinphos methyl	0	0	0
21	Coumaphos	0	0	0
22	Demeton-S	55.3	73.0	69.0
23	Demeton-O	57.6	28.3	21.7
24	Merphos	50.6	65.3	61.3
25	Ethion	58.2	82.7	86.0

[a] All experiments were performed with a 7.85-mL extraction vessel. The amount of sand extracted was 8 g. The spiking level was 3.75 µg/g per compound. The extraction conditions are specified in Footnotes b and c. A 50-µm ID x 60-cm length uncoated fused-silica restrictor (J&W Scientific) was used.

[b] Exp. 1 and 2: 250 atm/70°C/5 min static and continued at 250 atm/70°C/55 min dynamic; 300 µL acetone was added to spiked sand.

[c] Exp. 3: 200 atm/60°/45 min dynamic, no modifier.

extractions are plotted in Figure 5, those from the extractions with carbon dioxide modified with 10 percent methanol are given in Table 10 (Compounds 1-25) and also plotted in Figure 6.

Diazinon (Compound 8) was not recovered under any of these conditions, with or without methanol modifier. Mevinphos (Compound 2), dimethoate (Compound 7), fensulfothion (Compound 17), azinphos methyl (Compound 20), and coumaphos (Compound 21) were not recovered with carbon dioxide alone (Figure 5).However, these five compounds were recovered almost quantitatively (80 to 100 percent) with carbon dioxide modified with 10 percent methanol (Figure 6). On the other hand, phorate (Compound 6), demeton-S (Compound 22), and demeton-O (Compound 23), although recovered with carbon dioxide alone, were not recovered at all when carbon dioxide with 10 percent methanol was used. It is possible that these compounds hydrolyzed under the conditions used in the presence of methanol. Acetone did not have any effect when added in small amounts to the sample prior to extraction.

In addition to these 25 compounds, we spiked additional 22 organophosphorus pesticides (Table 10 Compounds 26-47) onto sand (8 g) at 2.5 μg/g and extracted the spiked sand samples with carbon dioxide modified with 10 percent methanol. The recoveries for these 22 compounds are plotted in Figure 7. Except for TEPP (Compound 29), which is known to decompose when analyzed by gas chromatography, all compounds were recovered almost quantitatively under the stated conditions. These results show that many organophosphorus pesticides can be extracted by SFE with either carbon dioxide or, more advantageously, carbon dioxide modified with 10 percent methanol.

5.1.3 Base/Neutral/Acidic Compounds

Forty-three base/neutral/acidic compounds were spiked on Florisil, sand, alumina, or silica matrices and the spiked samples were extracted with supercritical carbon dioxide with and without modifiers. The modifiers tested included methanol, acetone, and toluene. The modifiers were loaded directly into the extraction vessels containing the samples spiked with the target compounds (at the suggestion of Dr. Julia Wheeler of DuPont). The amount of modifier was set arbitrary at 200 μL per sample. Since the modifier was added to the extraction vessel and not to the extracting medium, the extraction vessel had to be pressurized (static mode) for 10 min prior to the transfer of the target compounds to the collection vessel. The results of these experiments are summarized in Tables 11 through 13 and indicate that:

- Addition of modifier to the sample is helpful in the sense that it gives an indication of whether the modifier will improve the extraction efficiency. Since the extraction efficiencies for the base/neutral/acidic compounds were very low, addition of the modifier to the extracting medium may be a better approach.

- An improvement in the recovery of the base/neutral/acidic compounds by adding an additional step in the method (i.e., increasing temperature to 70°C and pressure to 250 atm) was evident. However, the recoveries were still low for most of the compounds. Higher pressure and addition of modifier to the supercritical fluid were considered.

- Collection of the base/neutral/acidic compounds in hexane (Table 12) or methylene chloride (Table 14) is adequate.

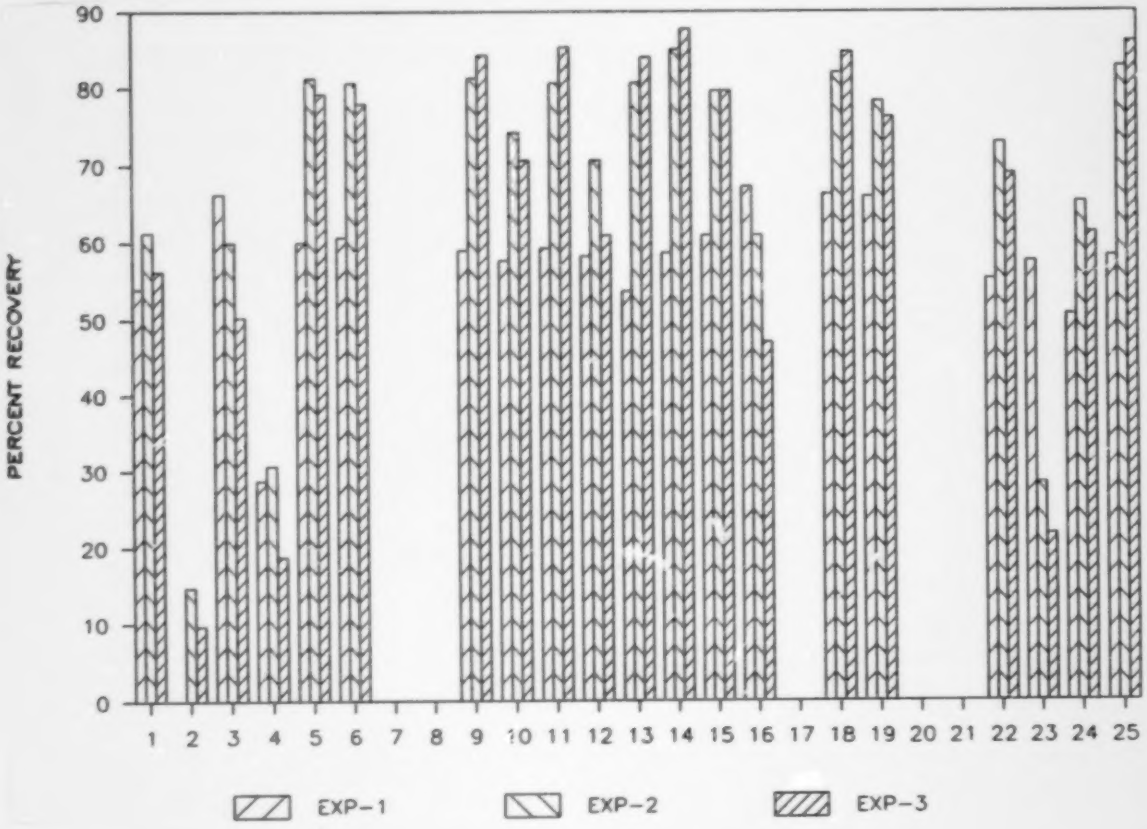


Figure 5. Percent recoveries of 25 organophosphorus pesticides extracted from spiked sand (8 g) with supercritical carbon dioxide. The experiments were performed using a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1 and Exp. 2: 250 atm/70°C/5 min static, 55 min dynamic; Exp. 3: 200 atm/60°C/45 min dynamic. Acetone (300 μL) was added to the soil in Exp. 1 and 2. The 25 organophosphorus pesticides are listed in the order in which they appear in Table 9.

TABLE 10. PERCENT RECOVERIES OF ORGANOPHOSPHORUS PESTICIDES FROM SPIKED SAND WITH SUPERCRITICAL CARBON DIOXIDE WITH 10 PERCENT METHANOL[a]

Compound no.	Compound	Exp. 1	Exp. 2	Exp. 3
1	Dichlorvos	97.6	96.7	95.5
2	Mevinphos	97.8	99.7	102
3	Ethoprop	83.5	82.3	91.4
4	Naled	22.9	14.5	4.8
5	Sulfotep	70.1	71.0	66.5
6	Phorate	0	0	0
7	Dimethoate	72.0	76.7	79.3
8	Diazinon	0	0	0
9	Disulfoton	78.2	77.7	73.9
10	Parathion methyl	89.1	90.9	98.0
11	Ronnel	94.0	97.7	92.8
12	Malathion	76.3	77.0	78.3
13	Fenthion	82.4	82.4	80.6
14	Chlorpyrifos	72.7	70.0	69.4
15	Parathion ethyl	86.8	87.6	91.8
16	Stirophos	87.1	116	92.3
17	Fensulfothion	82.9	117	93.8
18	Bolstar	78.2	105	80.8
19	EPN	83.3	83.9	88.7
20	Azinphos methyl	75.9	79.4	84.0
21	Coumaphos	77.3	78.7	81.7
22	Demeton-S	0	0	0
23	Demeton-O	0	0	0
24	Merphos	87.5	b	105
25	Ethion	78.4	80.7	82.0
26	Trimethyl phosphate	124	110	135
27	Hexamethyl phosphoramide	92.6	111	107
28	Trichlorfon	24.1	17.1	23.1
29	TEPP	6.0	9.9	5.0
30	Thionazin	84.5	74.9	84.0
31	Monocrotophos	54.9	59.4	70.6
32	Terbufos	80.5	81.0	81.1
33	Tricresyl phosphate	80.5	81.0	81.1

(continued)

[a] Each sample (8 g sand) was spiked with 1 mL of organophosphorus pesticide composite solution at 20 µg/mL. The extractions were performed in a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1 -- 150 atm/50°C/10 min static followed by 200 atm/60°C/ 10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2 -- 200 atm/60°C/30 min dynamic; Exp. 3 -- 250 atm/70°C/30 min dynamic.

[b] Data not available.

TABLE 10. (Concluded)[a]

Compound no.	Compound	Exp. 1	Exp. 2	Exp. 3
34	Fonophos	75.3	72.1	67.8
35	Dichlorphenthion	91.6	92.9	93.7
36	Phosphamidon	91.6	92.9	93.7
37	Methyl chlorpyrifos	79.6	77.2	73.2
38	Fenithrothion	85.7	92.1	83.8
39	Aspon	82.0	82.1	81.8
40	Trichloronate	82.0	82.1	81.8
41	Chlorfevinphos	81.6	101	83.4
42	Crotoxyphos	67.9	68.3	91.9
43	Tokuthion	79.7	78.9	78.4
44	Famphur	83.5	93.2	98.6
45	Phosmet	64.6	20.6	57.7
46	Leptophos	84.8	87.9	90.8
47	Azinphos ethyl	76.0	82.7	87.0

[a] Each sample (8 g sand) was spiked with 1 mL of organophosphorus pesticide composite solution at 20 μg/mL. The extractions were performed in a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1 -- 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2 -- 200 atm/60°C/30 min dynamic; Exp. 3 -- 250 atm/70°C/30 min dynamic.

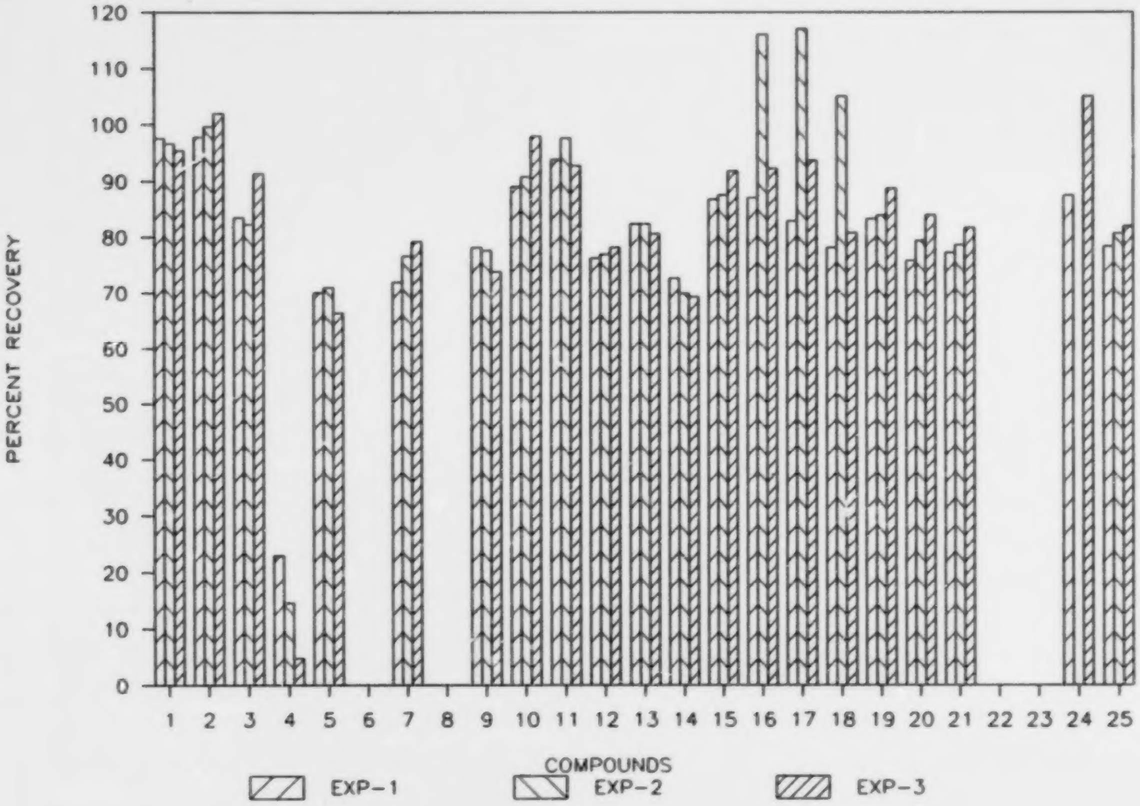


Figure 6. Percent recoveries of 25 organophosphorus pesticides extracted from spiked sand (8 g) with supercritical carbon dioxide with 10 percent methanol. The experiments were performed using a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1: 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2: 200 atm/60°C/30 min dynamic; Exp. 3: 250 atm/70°C/30 min dynamic. The 25 organophosphorus pesticides are listed in the order in which they appear in Table 10.

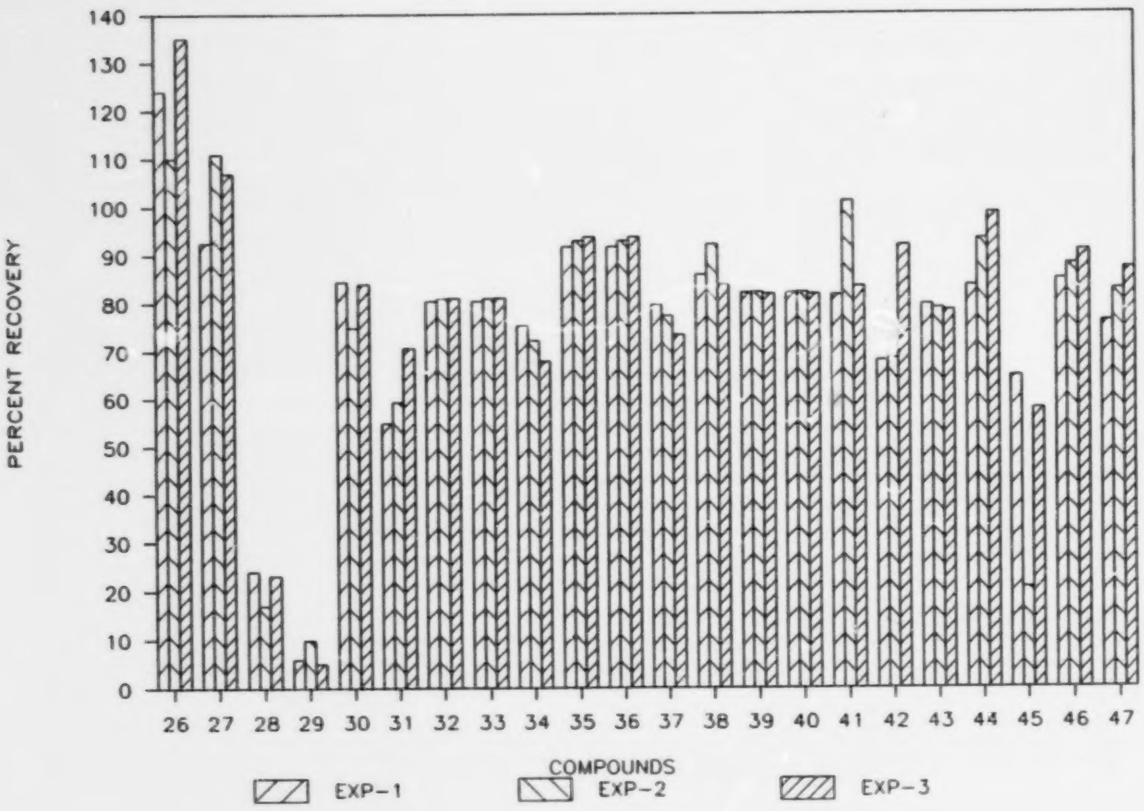


Figure 7. Percent recoveries of additional 22 organophosphorus pesticides extracted from spiked sand (8 g) with supercritical carbon dioxide with 10 percent methanol. The experiments were performed using a 7.85-mL extraction vessel. The conditions were as follows: Exp. 1: 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2: 200 atm/60°C/30 min dynamic; Exp. 3: 250 atm/70°C/30 min dynamic. The additional 22 organophosphorus pesticides (Compounds 26 through 47) are listed in the order in which they appear in Table 10.

TABLE 11. PERCENT RECOVERIES OF BASE/NEUTRAL/ACIDIC COMPOUNDS FROM SPIKED FLORISIL USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Without modifier			With 200 μL methanol		
		First extraction	Second extraction	Total	First extraction	Second extraction	Total
1	Phenol	3.0	2.4	5.4	8.4	1.9	10.3
2	Bis(2-chloroethyl)ether	7.2	6.1	13.3	13.1	7.2	20.3
3	2-Chlorophenol	11.0	8.7	19.7	10.1	8.7	18.8
4	1,3-Dichlorobenzene	7.1	25.2	32.3	16.4	3.1	19.5
5	1,4-Dichlorobenzene	5.4	27.9	33.3	18.5	3.2	21.7
6	Benzyl alcohol	0	0	0	6.8	9.8	16.6
7	1,2-Dichlorobenzene	11.0	23.2	34.2	16.5	5.3	21.8
8	2-Methylphenol	4.5	3.9	8.4	9.6	3.5	13.1
9	Bis(2-chloroisopropyl)ether	12.7	10.2	22.9	17.0	11.8	28.8
10	4-Methylphenol	2.7	2.4	5.1	9.0	1.7	10.7
11	N-nitroso-di-n-propylamine	0	0	0	12.7	0	10.7
12	Hexachloroethane	5.3	32.9	38.2	22.9	3.2	26.1
13	Nitrobenzene	7.5	6.4	13.9	13.1	6.4	19.5
14	Isophorone	0	0	0	0	0	0
15	2-Nitrophenol	8.3	7.8	16.1	13.3	7.5	20.8
16	2,4-Dimethylphenol	3.8	3.2	7.0	8.8	2.6	11.4
17	Benzoic acid	0	0	0	12.9	0	12.9
18	Bis(2-chloroethoxy)methane	4.2	3.3	7.5	12.4	4.2	16.6
19	2,4-Dichlorophenol	8.4	7.3	15.7	9.4	6.0	15.4
20	1,2,4-Trichlorobenzene	13.1	31.8	44.9	26.0	6.7	32.7
21	Hexachlorobutadiene	7.4	39.8	47.2	28.4	3.4	31.8
22	4-Chloro-3-methylphenol	2.1	2.0	4.1	7.8	1.0	8.8
23	2-Methylnaphthalene	21.9	22.7	44.6	22.1	11.5	33.6
24	Hexachlorocyclopentadiene	10.6	31.9	42.5	25.7	5.4	31.1
25	2,4,6-Trichlorophenol	6.7	7.9	14.6	9.3	5.7	15.0
26	2,4,5-Trichlorophenol	5.3	5.9	11.2	8.9	3.5	12.4
27	2-Chloronaphthalene	23.1	22.0	45.1	21.0	12.7	33.7
28	Dimethylphthalate	0	0	0	8.8	0	8.8
29	2,4-Dinitrophenol	0	0	0	0	0	0
30	4-Nitrophenol	0	2.1	2.1	4.3	0	4.3
31	Dibenzofuran	21.1	15.8	36.9	17.2	14.1	31.3
32	2,4-Dinitrotoluene	0	0	0	8.3	0	8.3
33	2,6-Dinitrotoluene	0	2.7	2.7	10.1	1.9	12.0
34	Diethylphthalate	0	0	0	9.1	0	9.1
35	4-Chlorophenyl-phenylether	21.1	16.4	37.5	18.1	13.1	31.2
36	4,6-Dinitro-2-methylphenol	0	0	0	0	0	0
37	4-Bromophenyl-phenylether	21.2	15.3	36.5	16.4	1.7	28.1
38	Hexachlorobenzene	21.8	16.6	48.4	15.0	10.9	25.9
39	Pentachlorophenol	0	0	0	2.0	0	2.0
40	Di-n-butylphthalate	0	0	0	10.1	0	10.1
41	Butylbenzylphthalate	0	0	0	9.9	0	9.9
42	Bis(2-ethylhexyl)phthalate	0	0	0	10.7	0	10.7
43	Di-n-octylphthalate	0	0	0	10.7	0	10.7

[a] The extraction conditions were as follows: 7.85-mL extraction vessel; 25-μm ID uncoated fused-silica tubing as restrictor; 50°C/150 atm/10 min static followed by 60°C/200 atm/10 min dynamic; the spiking level was 50 μg/g for base/neutral compounds and 100 μg/g for acidic compounds.

TABLE 12. PERCENT RECOVERIES OF BASE/NEUTRAL/ACIDIC COMPOUNDS FROM SPIKED FLORISIL USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Verification of collection efficiency[b]	Percent recovery from Florisil with supercritical carbon dioxide[a]		
			With 200 µL methanol	With 200 µL acetone	With 200 µL toluene
1	Phenol	123	7.8	13.1	6.7
2	Bis(2-chloroethyl)ether	103	13.1	30.2	14.8
3	2-Chlorophenol	112	21.9	22.6	19.1
4	1,3-Trichlorobenzene	104	76.3	59.0	40.7
5	1,4-Dichlorobenzene	102	79.4	63.6	43.8
6	Benzyl alcohol	103	1.8	8.9	0
7	1,2-Dichlorobenzene	105	66.8	56.0	40.2
8	2-Methylphenol	118	10.6	15.9	10.0
9	Bis(2-chloroisopropyl)ether	102	19.8	40.9	24.1
10	4-Methylphenol	109	5.9	11.3	5.6
11	N-Nitrosodi-n-propylamine	107	0	12.2	0
12	Hexachloroethane	106	83.0	65.5	49.5
13	Nitrobenzene	101	11.5	37.0	12.9
14	Isophorone	104	0	8.8	0
15	2-Nitrophenol	115	9.9	25.0	12.4
16	2,4-Dimethylphenol	122	7.6	14.7	7.2
17	Benzoic acid	120	0	0	0
18	Bis(2-chloroethoxy)methane	105	5.9	22.6	7.9
19	2,4-Dichlorophenol	115	17.9	14.8	14.8
20	1,2,4-Trichlorobenzene	101	66.6	58.4	41.0
21	Hexachlorobutadiene	99.2	67.8	56.5	40.7
22	4-Chloro-3-methylphenol	109	5.2	7.6	4.4
23	2-Methylnaphthalene	102	47.4	53.1	38.7
24	Hexachlorocyclopentadiene	104	62.7	53.9	37.3
25	2,4,6-Trichlorophenol	78.1	10.9	10.1	9.2
26	2,4,5-Trichlorophenol	76.3	10.7	9.9	9.0
27	2-Chloronaphthalene	99.0	47.9	52.1	38.7
28	Dimethylphthalate	101	0	6.5	0
29	2,4-Dinitrophenol	147	0	0	0
30	4-Nitrophenol	123	3.4	0	0
31	Dibenzofuran	101	34.2	43.3	31.0
32	2,4-Dinitrotoluene	102	1.3	12.7	0
33	2,6-Dinitrotoluene	103	5.0	22.3	6.3
34	Diethylphthalate	101	0	6.7	0
35	4-Chlorophenyl-phenylether	100	30.7	33.4	26.9
36	4,6-Dinitro-2-methylphenol	146	0	0	0
37	4-Bromophenyl-phenylether	103	25.7	28.1	23.3
38	Hexachlorobenzene	101	31.3	35.6	23.6
39	Pentachlorophenol	130	2.0	0	0
40	Di-n-butylphthalate	117	0.7	8.6	1.1
41	Butylbenzylphthalate	106	0	4.9	0
42	Bis(2-ethylhexyl)phthalate	104	0	8.0	0
43	Di-n-octylphthalate	109	0	6.2	0

[a] The extraction conditions were as follows: 7.85-mL extraction vessel; 25-µm ID uncoated fused-silica tubing as restrictor; 50°C/150 atm/10 min static followed by 60°C/200 atm/10 min dynamic followed by 70°C/250 atm/10 min dynamic; the spiking level was 50 µg/g for base/neutral compounds and 100 µg/g for acidic compounds.

[b] Collection solvent was hexane.

TABLE 13. PERCENT RECOVERIES OF BASE/NEUTRAL/ACIDIC COMPOUNDS FROM VARIOUS MATRICES WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Matrix: Florisil supercritical carbon dioxide	Matrix: sand[b] supercritical carbon dioxide		Matrix: alumina[b] supercritical carbon dioxide		Matrix: silica gel[b] supercritical carbon dioxide	
		250 atm/100°C time: 2 hrs	Without modifier	With modifier	Without modifier	With modifier	Without modifier	With modifier
1	Phenol	27.1	14.9	13.1	0	1.3	2.5	4.0
2	Bis(2-chloroethyl)ether	52.6	3.1	1.1	21.1	21.7	12.5	17.4
3	2-Chlorophenol	53.7	4.4	1.3	1.8	6.2	9.6	12.3
4	1,3-Dichlorobenzene	72.4	0	0	2.5	0	8.1	5.0
5	1,4-Dichlorobenzene	79.6	0	0	3.3	0	7.9	4.1
6	Benzyl alcohol	0	19.1	23.6	0	0	0	0
7	1,2-Dichlorobenzene	77.8	0	0	4.7	2.2	11.9	9.7
8	2-Methylphenol	35.7	17.0	16.7	0	2.4	3.6	5.6
9	Bis(2-chloroisopropyl)ether	59.3	5.3	1.7	40.2	40.2	21.6	30.6
10	4-Methylphenol	23.4	22.1	32.1	0	2.4	2.2	3.5
11	N-nitroso-di-n-propylamine	4.1	19.4	34.3	4.1	5.0	2.3	6.5
12	Hexachloroethane	75.6	0	0	0	0	9.3	0
13	Nitrobenzene	46.7	18.4	13.0	28.0	28.5	22.3	27.4
14	Isophorone	2.1	28.7	42.0	2.4	3.5	1.3	2.9
15	2-Nitrophenol	43.5	14.0	12.0	12.5	16.5	15.0	19.1
16	2,4-Dimethylphenol	27.5	24.3	38.1	0	0	3.5	5.2
17	Benzoic acid	0	0	0	0	0	0	0
18	Bis(2-chloroethoxy)methane	28.7	21.6	33.2	13.8	16.6	6.8	10.1
19	2,4-Dichlorophenol	54.1	19.8	27.7	0	1.8	5.6	6.9
20	1,2,4-Trichlorobenzene	82.1	7.4	1.7	19.9	15.4	23.6	20.2
21	Hexachlorobutadiene	82.5	0	0	17.9	12.9	20.0	15.7
22	4-Chloro-3-methylphenol	19.7	22.3	49.3	0	0	0.9	1.2
23	2-Methylnaphthalene	79.1	22.2	22.8	35.3	38.5	32.8	31.9
24	Hexachlorocyclopentadiene	79.3	12.3	8.9	24.2	25.5	35.9	32.5
25	2,4,6-Trichlorophenol	58.1	26.2	55.7	0	1.5	3.6	9.2
26	2,4,5-Trichlorophenol	63.2	28.6	62.2	0	1.7	2.3	5.4
27	2-Chloronaphthalene	74.7	27.0	40.4	34.8	43.3	32.3	32.6
28	Dimethylphthalate	1.9	25.2	51.5	2.6	3.9	1.3	3.6
29	2,4-Dinitrophenol	0	10.6	29.6	0	0	0	0
30	4-Nitrophenol	4.8	8.4	6.2	0	0	0	0
31	Dibenzofuran	66.7	30.9	64.0	31.8	38.6	28.0	30.2
32	2,4-Dinitrotoluene	6.3	28.4	57.1	5.3	7.9	4.6	6.3
33	2,6-Dinitrotoluene	20.1	31.7	69.0	8.8	13.4	6.9	9.8
34	Diethylphthalate	1.7	25.9	58.7	2.6	3.3	1.3	3.6
35	4-Chlorophenyl-phenylether	67.0	28.4	69.2	37.1	39.8	26.8	30.4
36	4,6-Dinitro-2-methylphenol	0	18.4	42.8	0	0	0	3.2
37	4-Bromophenyl-phenylether	59.6	26.1	66.2	28.7	31.8	20.9	23.8
38	Hexachlorobenzene	63.3	28.9	56.7	37.0	40.7	28.9	31.5
39	Pentachlorophenol	10.0	15.8	39.5	0	0	0	0
40	Di-n-butylphthalate	1.8	28.3	64.7	3.3	4.5	1.9	5.2
41	Butylbenzylphthalate	0	24.0	49.5	0	2.1	0	2.4
42	Bis(2-ethylhexyl)phthalate	0.8	27.6	68.4	3.7	4.1	1.7	5.1
43	Di-n-octylphthalate	0.5	27.3	56.8	2.9	3.4	1.2	4.1

---

[a] The extraction conditions were as follows: 7.85-mL extraction vessel; 25-µm ID uncoated fused-silica tubing as restrictor. Modifier (200 µL acetone) was added to the spiked matrix. The amounts of sample loaded to the extraction vessel were 9.0 g for sand, 7.0 for alumina, and 3.5 g for silica gel. Each matrix was spiked with 100 µL of 2 µg/µL (base/neutral compounds) or 200 µL of 2 µg/µL (acidic compounds).

[b] The extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic.

TABLE 14. VERIFICATION OF COLLECTION EFFICIENCY USING METHYLENE CHLORIDE AS COLLECTION SOLVENT[a]

Compound no.	Compound	SFE-Blank 1	SFE-Blank 2
1	Phenol	82.1	107
2	Bis(2-chloroethyl)ether	85.9	102
3	2-Chlorophenol	93.9	101
4	1,3-Dichlorobenzene	107	93.0
5	1,4-Dichlorobenzene	89.8	98.1
6	Benzyl alcohol	39.7	64.8
7	1,2-Dichlorobenzene	98.2	92.2
8	2-Methylphenol	86.8	96.7
9	Bis(2-chloroisopropyl)ether	77.6	105
10	4-Methylphenol	63.7	94.3
11	N-Nitroso-di-n-propylamine	84.9	108
12	Hexachloroethane	90.1	94.1
13	Nitrobenzene	101	146
14	Isophorone	88.9	104
15	2-Nitrophenol	99.0	91.9
16	2,4-Dimethylphenol	75.5	83.6
17	Benzoic acid	76.7	86.9
18	Bis(2-chloroethoxy)methane	92.0	97.6
19	2,4-Dichlorophenol	78.2	92.9
20	1,2,4-Trichlorobenzene	112	99.1
21	Hexachlorobutadiene	105	98.6
22	4-Chloro-3-methylphenol	83.3	94.3
23	2-Methylnaphthalene	101	97.4
24	Hexachlorocyclopentadiene	121	104
25	2,4,6-Trichlorophenol	105	114
26	2,4,5-Trichlorophenol	89.3	92.9
27	2-Chloronaphthalene	115	114
28	Dimethylphthalate	89.1	110
29	2,4-Dinitrophenol	131	102

(continued)

[a] The experiment was performed by spiking the compounds into the collection vial containing 5 mL methylene chloride and purging the system with carbon dioxide containing 10 percent methanol under the following conditions:
SFE-Blank 1: 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/10 min dynamic
SFE-Blank 2: 250 atm/70°C/30 min dynamic.
The spiking level was 200 µg for base/neutral compounds, 400 µg for the acidic compounds, and 200 µg for the surrogates.

TABLE 14. (Concluded)

Compound no.	Compound	SFE-Blank 1	SFE-Blank 2
30	4-Nitrophenol	58.6	54.5
31	Dibenzofuran	109	110
32	2,4-Dinitrotoluene	99.7	110
33	2,6-Dinitrotoluene	91.5	115
34	Diethylphthalate	86.3	100
35	4-Chlorophenyl-phenylether	109	112
36	4,6-Dinitro-2-methylphenol	105	97.1
37	4-Bromophenyl-phenylether	98.1	109
38	Hexachlorobenzene	101	111
39	Pentachlorophenol	104	114
40	Di-n-butylphthalate	85.9	104
41	Butylbenzylphthalate	93.7	111
42	Bis(2-ethylhexyl)phthalate	96.5	114
43	Di-n-octylphthalate	102	119
44	Nitrobenzene-d_5	93.0	102
45	2-Fluorobiphenyl	109	109
46	Phenol-d_5	91.5	101
47	2-Fluorophenol	94.8	106
48	2,4,6-Tribromophenol	93.4	107
49	Terphenyl-d_{14}	103	113

[a] The experiment was performed by spiking the compounds into the collection vial containing 5 mL methylene chloride and purging the system with carbon dioxide containing 10 percent methanol under the following conditions:

SFE-Blank 1: 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic,
250 atm/70°C/10 min dynamic
SFE-Blank 2: 250 atm/70°C/30 min dynamic.

The spiking level was 200 μg for base/neutral compounds, 400 μg for the acidic compounds, and 200 μg for the surrogates.

Table 15 lists the recoveries of the 43 base/neutral/acidic compounds from spiked sand. When using a 50-μm ID restrictor in place of the 25-μm ID restrictor and performing the extraction at higher pressures, the recoveries of some compounds were quite low. We believe that the ethers, the chlorinated benzenes, hexachloroethane, and hexachlorobutadiene are extracted; however, because these compounds are very volatile, they are probably partially lost from the collection vial through volatilization. Benzoic acid was not recovered, and 2,4-dinitrophenol and the phthalate esters recoveries were low when supercritical carbon dioxide was used for extraction. Addition of 200 μL acetone as modifier did not improve the recoveries.

Experiments performed with only the acidic compounds indicate excellent recoveries when the extraction was performed with supercritical carbon dioxide at 350 atm/60°C for 20 min (Table 16 and Figure 8). The sand sample used in this case was very clean as demonstrated by the results in Table 17 and the GC/MS chromatogram shown in Figure 9 (the various peaks shown in the GC/MS chromatogram correspond to the five surrogates spiked in the sample prior to extraction and the six internal standards spiked in the extract prior to GC/MS analysis). The lowest recoveries in this case were found for phenol (57.7 percent) and the two similar surrogates, 2-fluorophenol and phenol-d_5, at 53.2 and 60.1, respectively. Nonetheless, these extraction efficiencies are higher than the ones currently listed in the EPA Method 3550.

The group of five surrogate compounds listed in Tables 16 and 17 were spiked in samples for which the SFE extracts were analyzed by GC/MS. Overall, the recoveries of the surrogate compounds ranged from approximately 50 to 85 percent. These recoveries were considered acceptable and the group of five surrogate compounds was recommended for incorporation into the SFE protocol.

5.1.4 PAHs

Sixteen PAHs were spiked on sand, urban dust, coal, and coal fly ash (Tables 18 and 19). Average recoveries after extraction with supercritical carbon dioxide at 150 atm/50°C/60 min were almost quantitative for 1-g samples of coal and coal fly ash, but only 57 percent for the 1-g urban dust sample. Average recoveries for the spiked sand samples (approximately 10 g each) under two sets of conditions improved with added modifier (200 μL acetone, added to the spiked sample) from 73.6 to 81.1 percent in one case and from 58.0 to 88.8 percent in the other case. Two fractions were collected for each sample to verify the completeness of the extraction. GC/MS chromatograms obtained for each matrix are shown in Figures 10 through 18.

5.1.5 Standard Reference Materials

Three standard reference materials certified for PAHs were extracted with supercritical carbon dioxide modified with 10 percent methanol or supercritical carbon dioxide alone. The results for the PAH-contaminated soil, identified as Fisher Scientific SRS 103-100, are presented in Table 20. This soil was certified for 15 compounds at concentrations ranging from 19.1 to 1,618 ppm. The values reported in Table 20 represent the sums of concentrations found in nine fractions that were collected from a 6-g sample over a period of 270 min. The results show that only five compounds gave acceptable recoveries (> 80 percent), whereas more than half of the recoveries were below 50 percent. Figures 19 through 27 show GC/MS chromatograms of each of the nine fractions collected from SRS 103-100. Replicate extractions performed on this standard reference soil (Table 21) indicate encouraging results for this matrix. Addition of water to the matrix prior to extraction appeared to have improved recoveries.

TABLE 15. PERCENT RECOVERIES OF BASE/NEUTRAL/ACIDIC COMPOUNDS FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Supercritical carbon dioxide	Supercritical carbon dioxide with 200 µL acetone
1	Phenol	141	83.5
2	Bis(2-chloroethyl)ether	37.6	36.3
3	2-Chlorophenol	73.1	57.9
4	1,3-Dichlorobenzene	3.9	1.9
5	1,4-Dichlorobenzene	4.6	2.1
6	Benzyl alcohol	111	128
7	1,2-Dichlorobenzene	9.0	5.0
8	2-Methylphenol	111	129
9	Bis(2-chloroisopropyl)ether	45.1	42.8
10	4-Methylphenol	148	96.6
11	N-nitroso-di-n-propylamine	57.6	67.1
12	Hexachloroethane	5.7	0
13	Nitrobenzene	59.4	54.9
14	Isophorone	59.1	73.6
15	2-Nitrophenol	67.0	55.3
16	2,4-Dimethylphenol	93.3	71.7
17	Benzoic acid	0	0
18	Bis(2-chloroethoxy)methane	65.7	83.3
19	2,4-Dichlorophenol	104	75.7
20	1,2,4-Trichlorobenzene	42.9	36.7
21	Hexachlorobutadiene	36.9	29.6
22	4-Chloro-3-methylphenol	176	113
23	2-Methylnaphthalene	74.2	72.1
24	Hexachlorocyclopentadiene	67.9	63.3
25	2,4,6-Trichlorophenol	105	88.5
26	2,4,5-Trichlorophenol	121	96.1
27	2-Chloronaphthalene	81.1	82.0
28	Dimethylphthalate	49.0	71.1
29	2,4-Dinitrophenol	33.1	26.8
30	4-Nitrophenol	82.7	111
31	Dibenzofuran	89.1	92.3
32	2,4-Dinitrotoluene	71.9	87.5
33	2,6-Dinitrotoluene	87.8	85.0
34	Diethylphthalate	48.5	72.5
35	4-Chlorophenyl-phenylether	83.6	90.1
36	4,6-Dinitro-2-methylphenol	49.6	53.3
37	4-Bromophenyl-phenylether	102	80.0
38	Hexachlorobenzene	113	79.9
39	Pentachlorophenol	66.4	58.2
40	Di-n-butylphthalate	51.9	77.8
41	Butylbenzylphthalate	32.1	63.3
42	Bis(2-ethylhexyl)phthalate	59.6	73.6
43	Di-n-octylphthalate	35.0	69.7

[a] All experiments were performed with a 7.85-mL extraction vessel. Extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. A 50-µm ID x 60-cm length uncoated fused-silica restrictor was used. Modifier (200 µL) was added to the spiked matrix. 9.3 g sand sandwiched between two plugs of regular glass wool was used in each experiment. Spiking levels of base/neutral/acidic compounds were 21.5 µg/g for the neutrals, and 18 µg/g per compound for the acidic compounds, except for 4-methylphenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol which were spiked at 3.6 µg/g per compound.

TABLE 16. PERCENT RECOVERIES OF ACIDIC COMPOUNDS FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound	Concentration found (μg/g)	Percent recovery
Phenol	57.7	57.7
2-Chlorophenol	77.4	77.4
2-Methylphenol	70.4	70.4
4-Methylphenol	76.2	76.2
2-Nitrophenol	75.7	75.7
2,4-Dimethylphenol	98.0	98.0
Benzoic acid	ND[b]	0
2,4-Dichlorophenol	84.3	84.3
4-Chloro-3-methylphenol	92.2	92.2
2,4,6-Trichlorophenol	83.4	83.4
2,4,5-Trichlorophenol	85.0	85.0
2,4-Dinitrophenol	85.9	85.9
4-Nitrophenol	81.6	81.6
4,6-Dinitro-2-methylphenol	93.4	93.4
Pentachlorophenol	89.0	89.0
Surrogate recovery		
2-Fluorophenol		53.2
Phenol-d_5		60.1
Nitrobenzene-d_5		73.2
2-Fluorobiphenyl		75.8
2,4,6-Tribromophenol		75.1

[a] The spiking level was 100 μg/g. The experiments were performed with supercritical carbon dioxide at 350 atm/60°C/20 min dynamic. The sample size was 2 g.

[b] Not detected; estimated detection limit 10 μg/g.

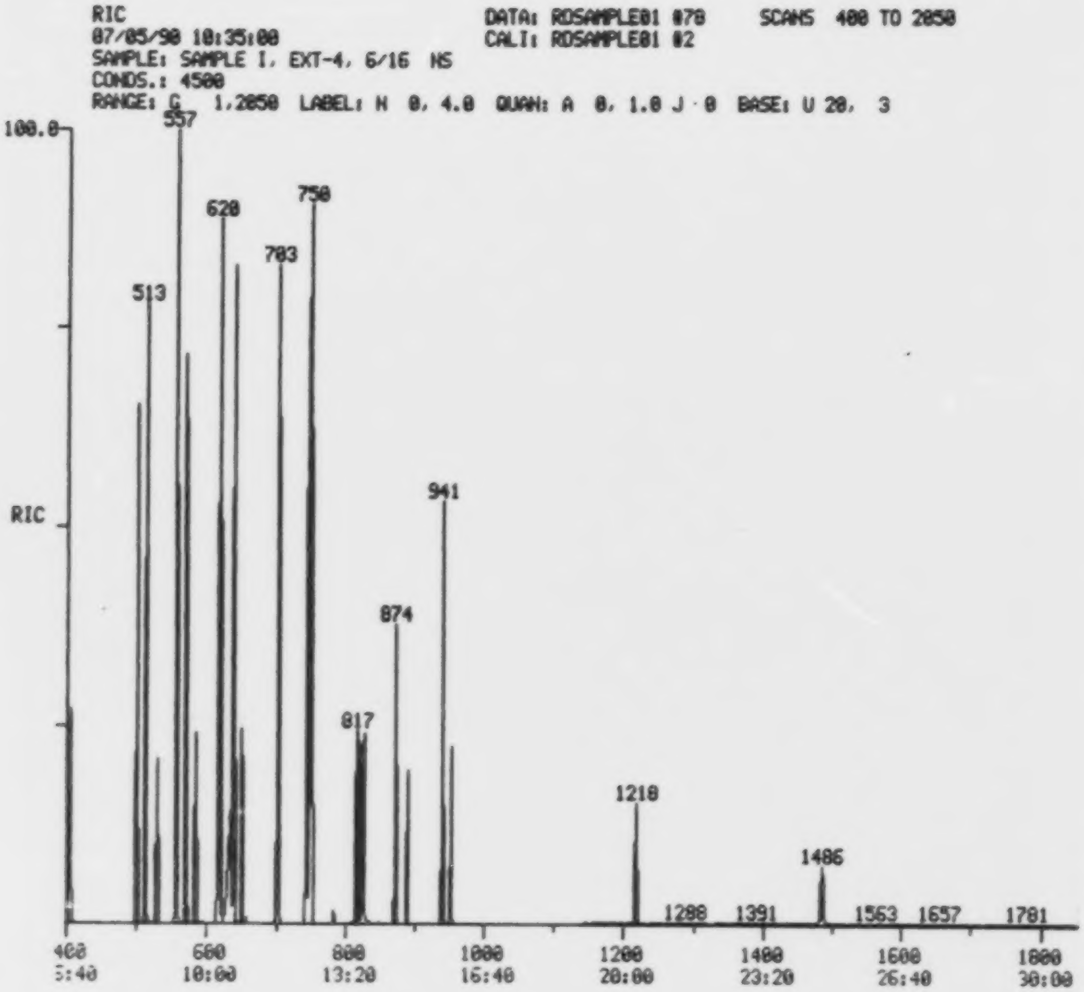
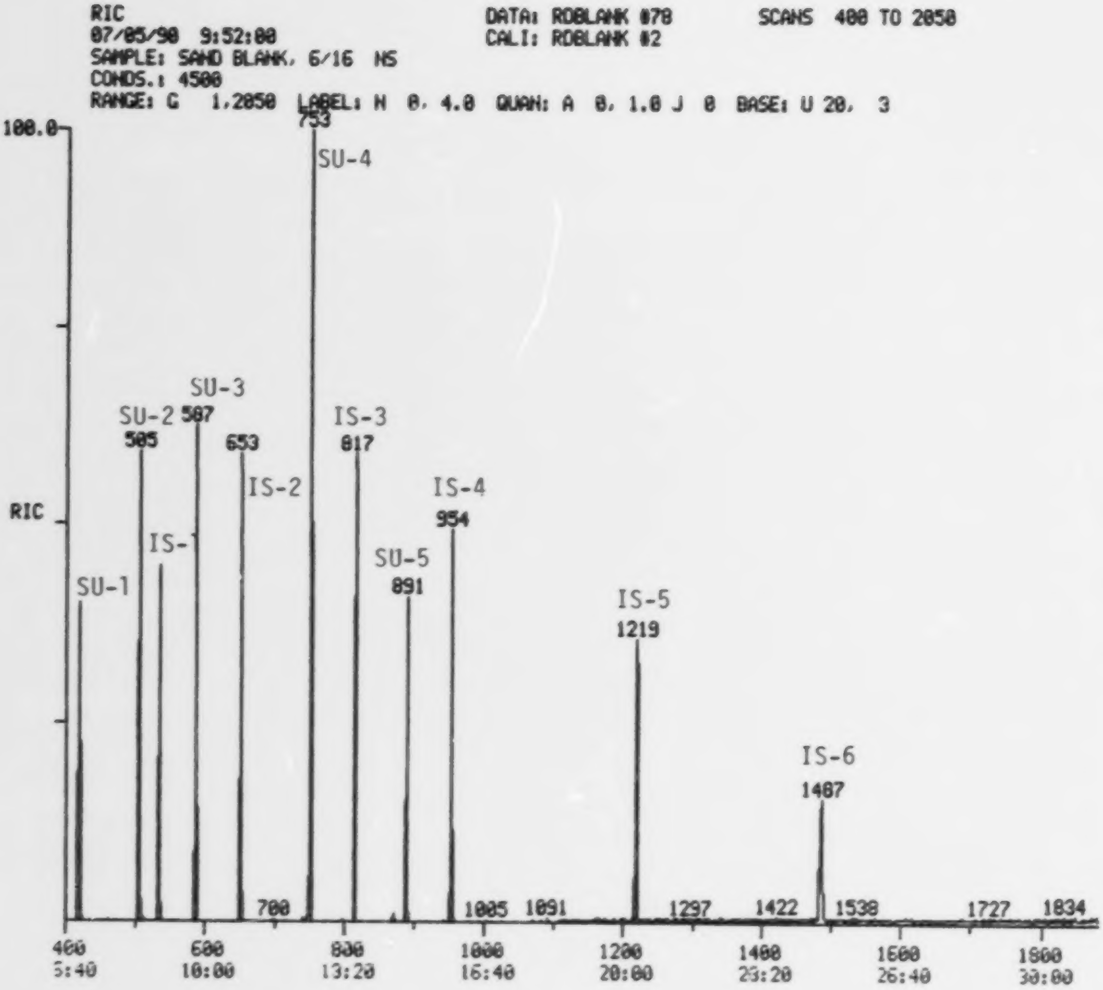


Figure 8. GC/MS chromatogram of extract from sand sample spiked with 15 phenols.

TABLE 17. RESULTS OF GC/MS ANALYSIS OF SAND SAMPLE EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound	Concentration found (μg/g)	Percent recovery
Fluoranthene	0.15	
Pyrene	0.25	
Surrogate recovery		
2-Fluorophenol		51.3
Phenol-d_5		64.0
Nitrobenzene-d_5		69.6
2-Fluorobiphenyl		81.5
2,4,6-Tribromophenol		74.2

[a] The experiments were performed with supercritical carbon dioxide at 350 atm/60°C/20 min dynamic. The sample size was 2 g. This was a blank sand sample spiked only with the surrogates. The spiking level of the surrogates was 50 μg/g per compound.



```
RIC                                             DATA: RDBLANK #78        SCANS  400 TO 2050
07/05/90  9:52:00                               CALI: RDBLANK #2
SAMPLE: SAND BLANK, 6/16  MS
CONDS.: 4500
RANGE: G   1,2050  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 9. GC/MS chromatogram of sand sample extract.

TABLE 18. PERCENT RECOVERIES OF PAHs FROM SPIKED SAND USING SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	150 atm/50°C/60 min First extraction	150 atm/50°C/60 min Second extraction	150 atm/50°C/60 min (with 200 µL acetone)
1	Naphthalene	41.0	0	86.2
2	Acenaphthylene	62.7	0	92.9
3	Acenaphthene	65.9	0	88.7
4	Fluorene	68.6	0	89.1
5	Phenanthrene	63.0	0	91.8
6	Anthracene	64.4	0	88.1
7	Fluoranthene	64.2	0.8	87.6
8	Pyrene	69.5	2.5	89.9
9	Benzo(a)anthracene	77.0	10.4	88.8
10	Chrysene	66.3	10.5	89.2
11	Benzo(b)fluoranthene	70.2	12.6	88.5
12	Benzo(k)fluoranthene	62.9	14.7	88.6
13	Benzo(a)pyrene	67.2	8.6	92.3
14	Indeno(1,2,3-c,d)pyrene	50.7	6.9	87.2
15	Dibenzo(a,h)anthracene	17.9	0	84.9
16	Benzo(g,h,i)perylene	16.6	0	87.0
	Terphenyl-d_{14} (surrogate)	87.5	94.5	69.5

[a] All experiments were performed with a 7.85-mL extraction cell. Modifier (200 µL) was added to the spiked matrix. 11.2 g sand was used for each experiment. The spiking level of PAHs was 200 µg per 11.2 g sand (100 µL of a methylene chloride solution at 2 µg/µL was spiked in each case). A 50-µm ID x 60-cm length uncoated fused-silica restrictor was used.

TABLE 19. PERCENT RECOVERIES OF PAHs FROM SPIKED SAND AND SPIKED NIST STANDARD REFERENCE MATERIALS USING SUPERCRITICAL CARBON DIOXIDE

	Compound	Sand[a] (9.3 g)	Sand with 200 µL acetone[b] (9.3 g)	Sand[b] (11.2 g)	Sand with 200 µL acetone[b] (11.2 g)	SRM-1649 Urban dust[c] (1 g)	SRM-1632a Coal[c] (1 g)	SRM-1633a Coal fly ash[c] (1 g)
1	Naphthalene	67.2	80.4	41.0	86.2	100	95.0	88.3
2	Acenaphthylene	81.7	78.4	62.7	92.9	95.3	92.8	88.8
3	Acenaphthene	87.8	81.2	65.9	88.7	104	93.0	89.5
4	Fluorene	86.7	80.2	68.6	89.1	101	94.6	89.2
5	Phenanthrene	85.7	79.0	63.0	91.8	118	95.0	87.5
6	Anthracene	84.6	77.5	64.4	88.1	93.8	91.7	85.7
7	Fluroanthene	85.7	78.4	64.2	87.6	88.8	92.6	90.7
8	Pyrene	89.3	82.7	69.5	89.9	70.0	94.8	87.4
9	Benzo(a)anthracene	85.8	82.1	77.0	88.8	14.5	96.7	88.6
10	Chrysene	76.8	82.6	66.3	89.2	26.7	96.7	88.6
11	Benzo(b)fluroanthene	97.0	83.5	70.2	88.5	20.0	104	88.1
12	Benzo(k)fluoranthene	63.7	84.1	62.9	88.6	30.0	98.9	100
13	Benzo(a)pyrene	70.4	81.7	67.2	92.3	19.2	100	92.7
14	Indeno(,2,3-c,d)pyrene	59.5	85.3	50.7	87.2	16.4	99.0	90.1
15	Dibenzo(a,h)anthracene	31.8	80.8	17.9	84.9	15.0	93.9	88.1
16	Benzo(g,h,i)perylene	24.3	79.9	16.6	87.0	12.8	93.8	85.2

[a] The extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. Single determination. Modifier (200 µL) was added to the spiked matrix (when applicable). The spiking level was 21.5 µg/g per compound.

[b] The extraction was performed at 150 atm/50°C/5 min static followed by 150 atm/50°C/55 min dynamic. Single determination. The spiking level was 21.5 µg/g per compound for the 9.3-g sample, and 17.9 µg/g per compound for the 11.2-g sample.

[a] The extraction was performed at 150 atm/50°C/5 min static followed by 150 atm/50°C/55 min dynamic. No compound were collected from the second extraction that was performed at 200 C/10 min dynamic followed by 250 C/10 min dynamic. Single determination. The spiking level was 200 µg/g per compound.

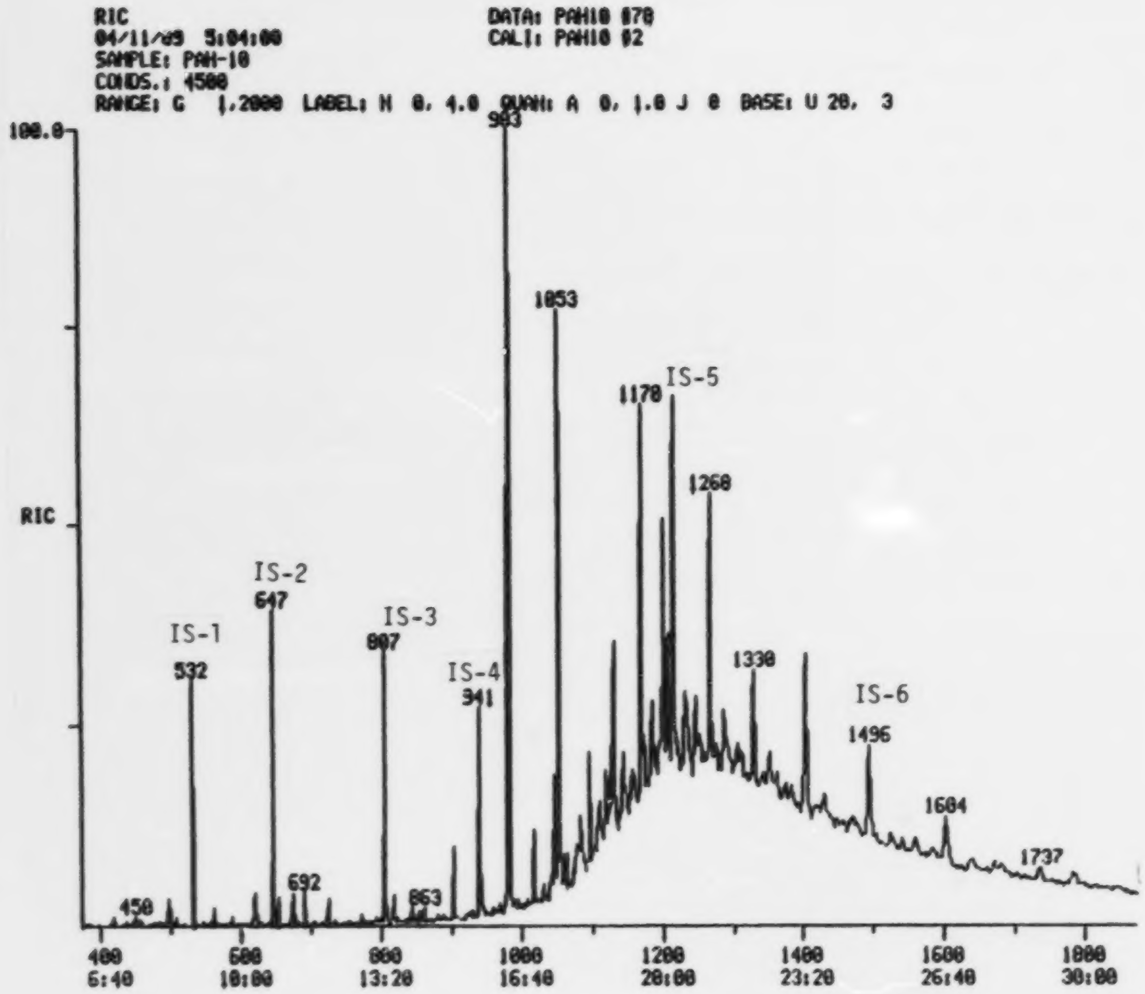


Figure 10. GC/MS chromatogram of urban dust sample (NIST SRM 1649) extract -- Fraction 1.

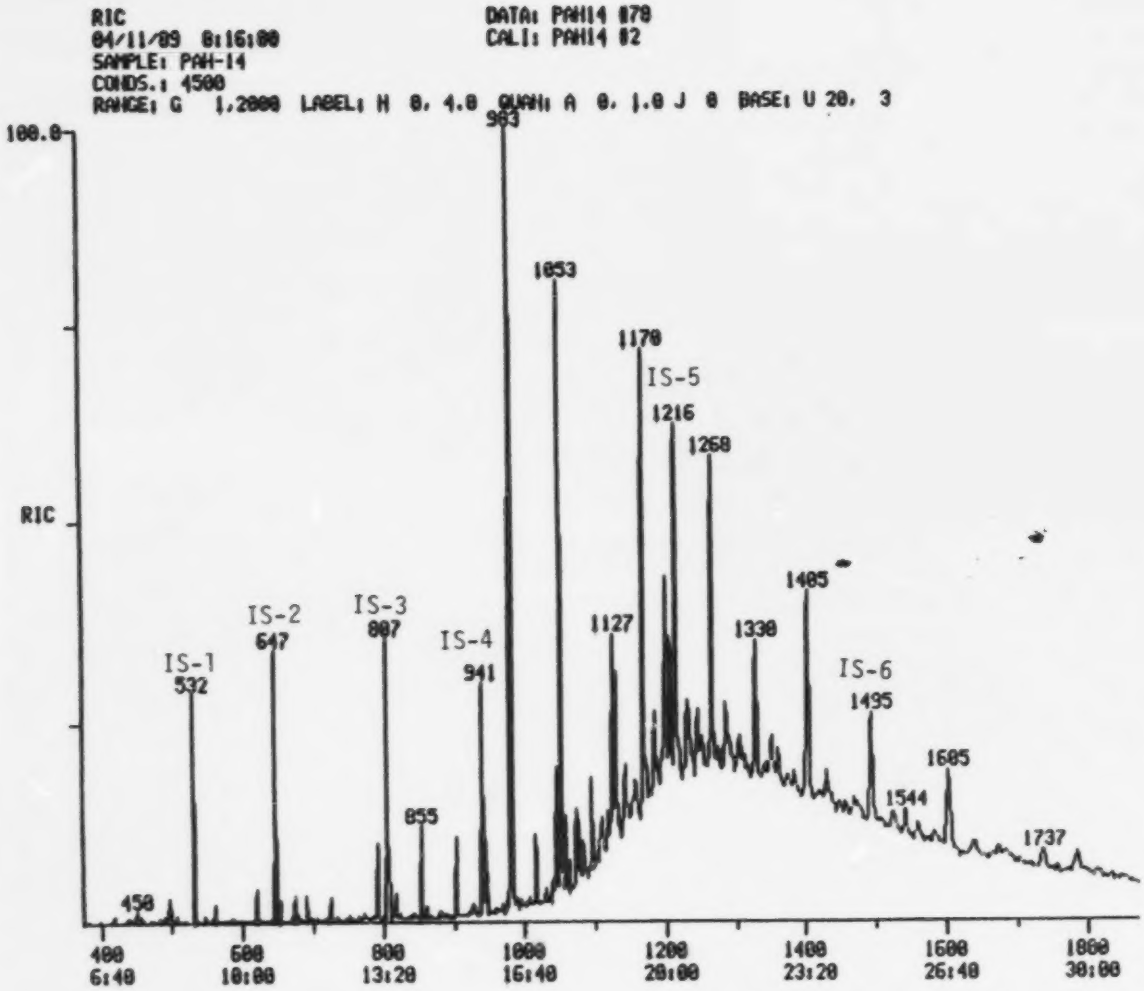


Figure 11. GC/MS chromatogram of extract of urban dust sample (NIST SRM 1649) spiked with PAHs -- Fraction 1.

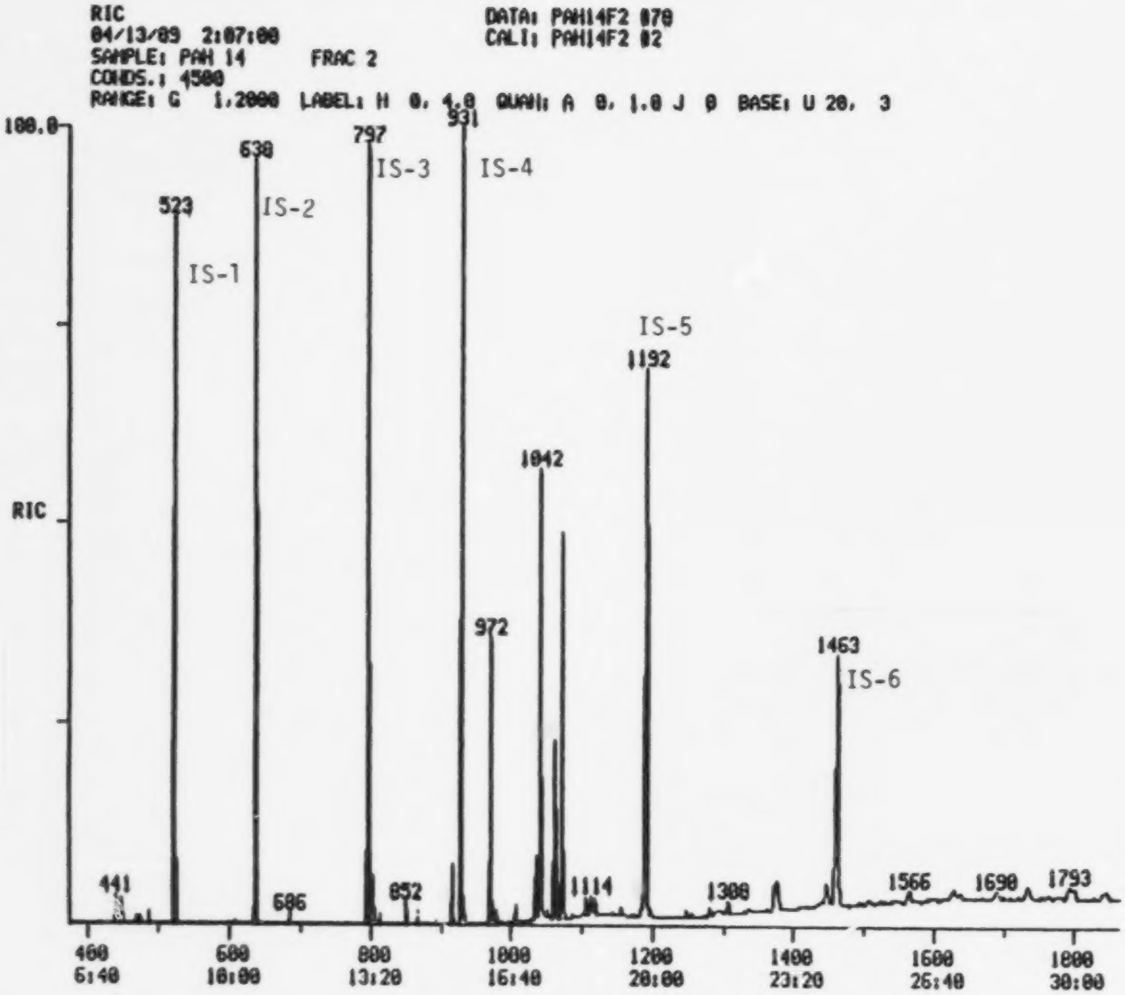


Figure 12. GC/MS chromatogram of extract of urban dust sample (NIST SRM 1649) spiked with PAHs -- Fraction 2.

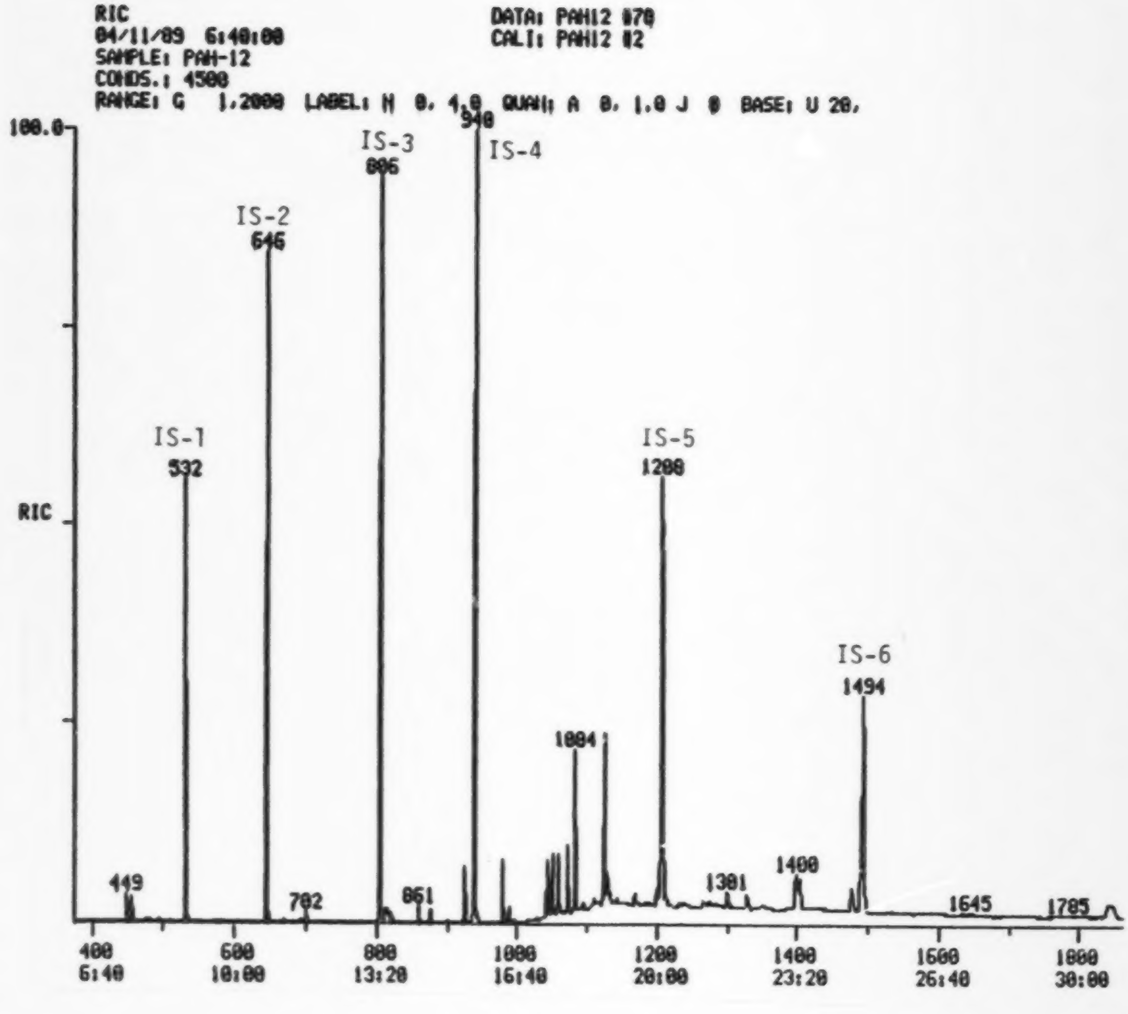


Figure 13. GC/MS chromatogram of coal fly ash sample (NIST SRM 1633a) extract -- Fraction 1.

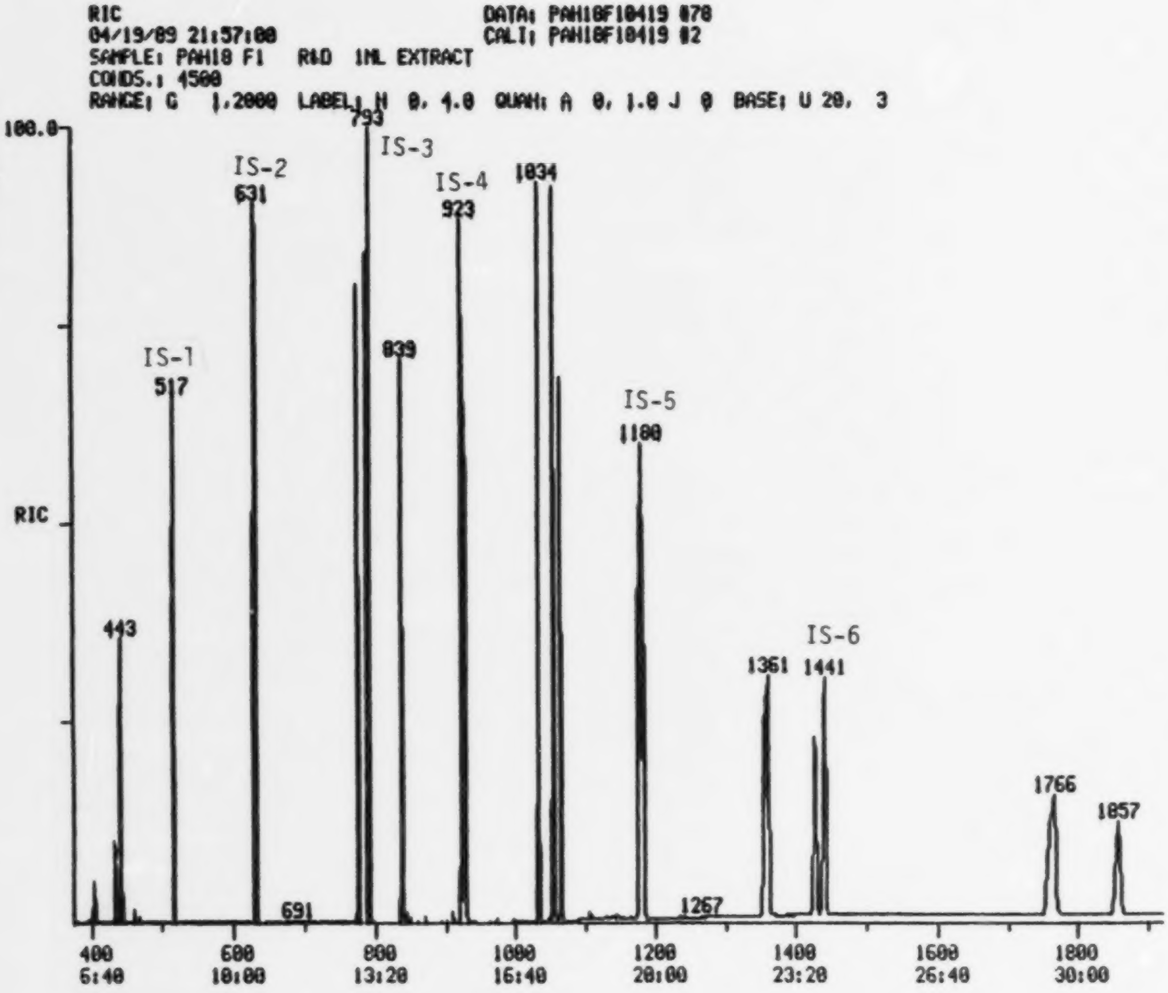


Figure 14. GC/MS chromatogram of extract of coal fly ash sample (NIST SRM 1633a) spiked with PAHs -- Fraction 1.

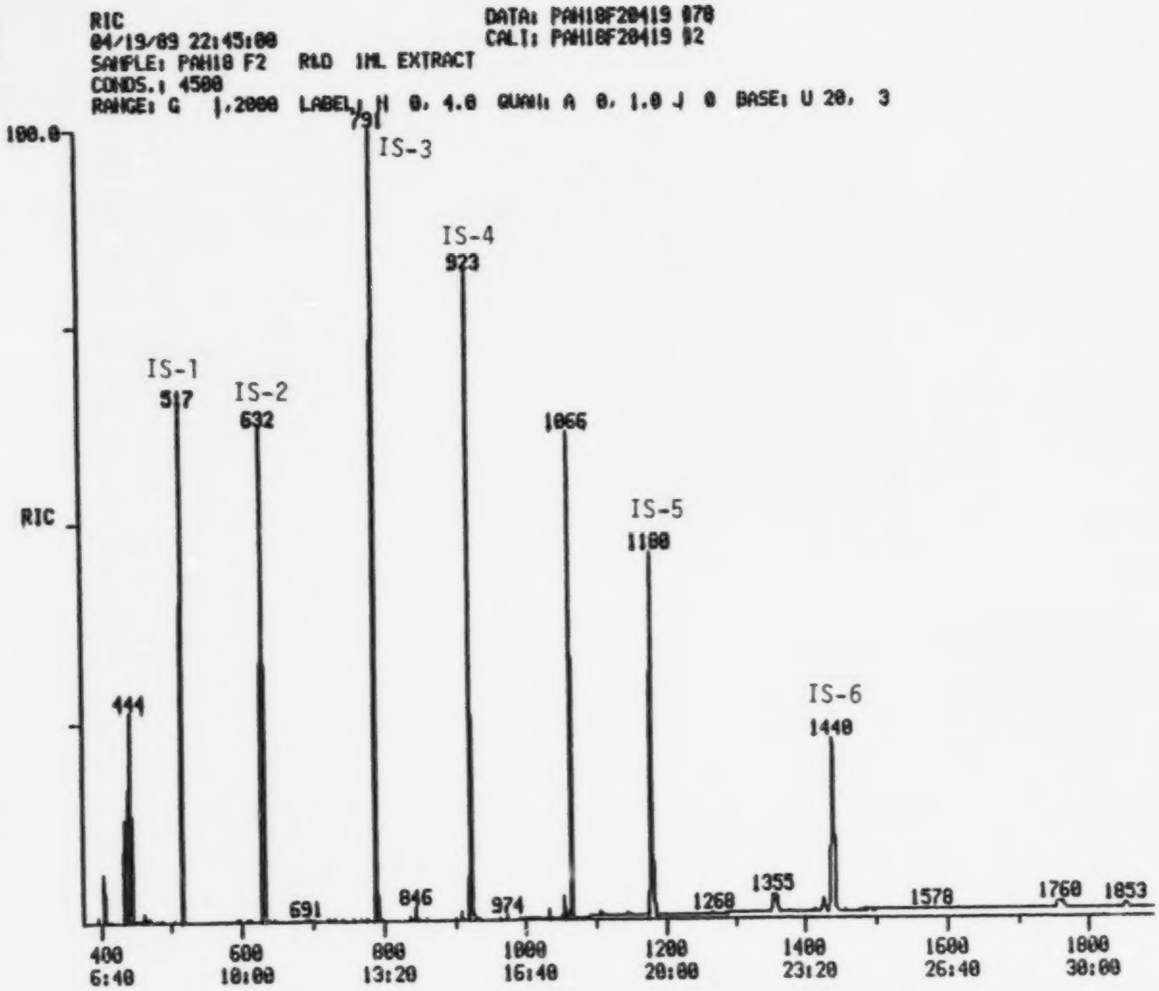


Figure 15. GC/MS chromatogram of extract of coal fly ash sample (NIST SRM 1633a) spiked with PAHs -- Fraction 2.

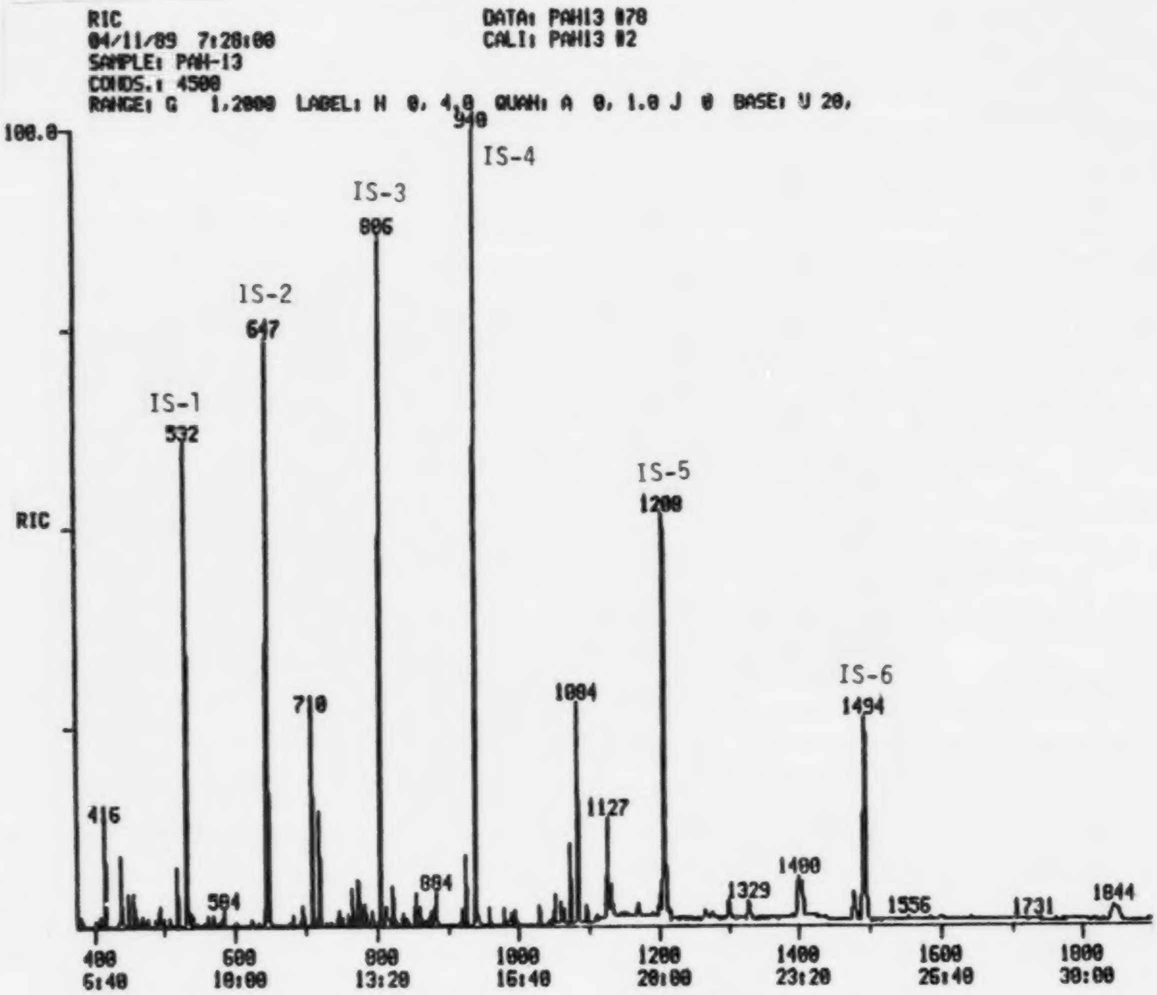


Figure 16. GC/MS chromatogram of coal sample (NIST SRM 1632a) extract -- Fraction 1.

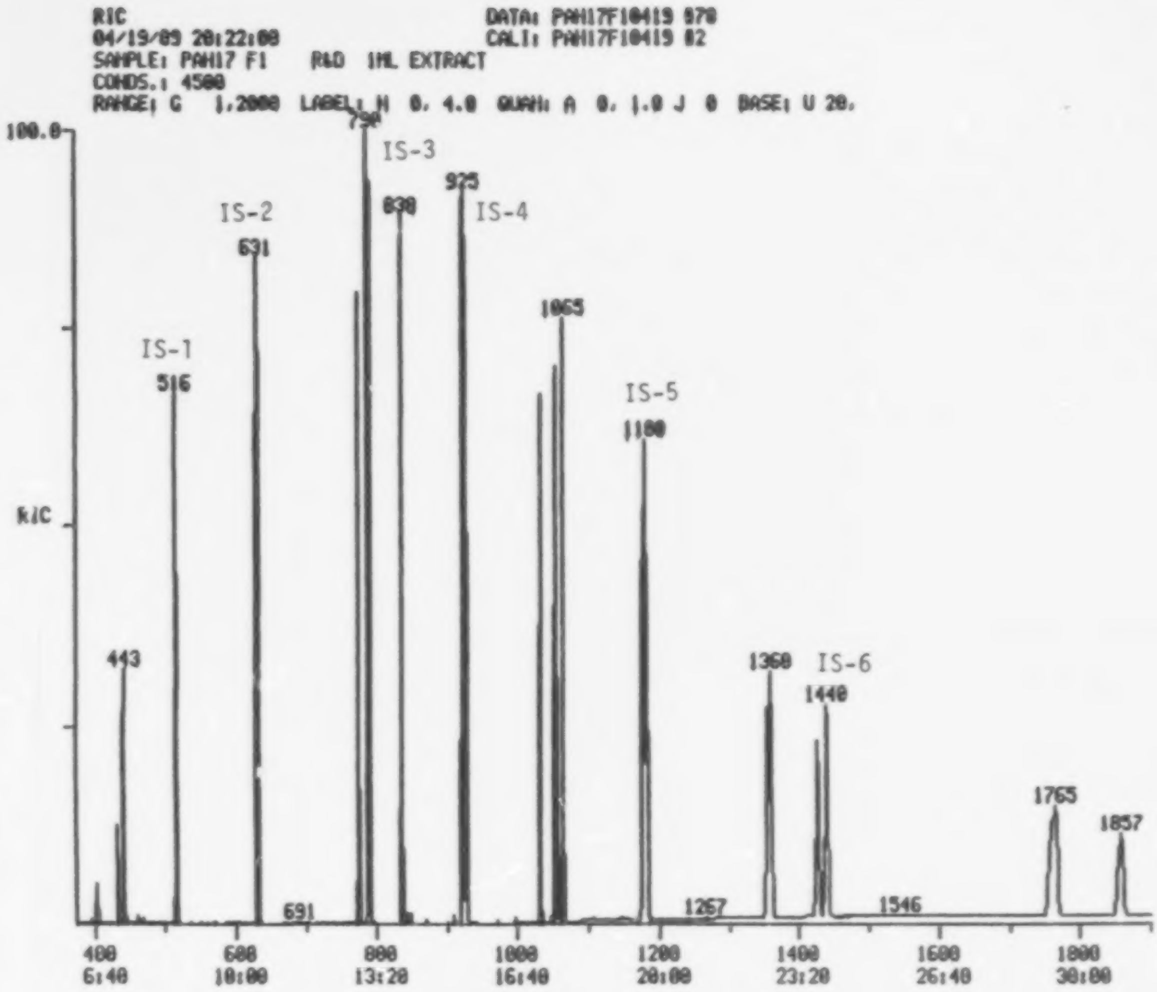


Figure 17. GC/MS chromatogram of extract of coal sample (NIST SRM 1632a) spiked with PAHs -- Fraction 1.

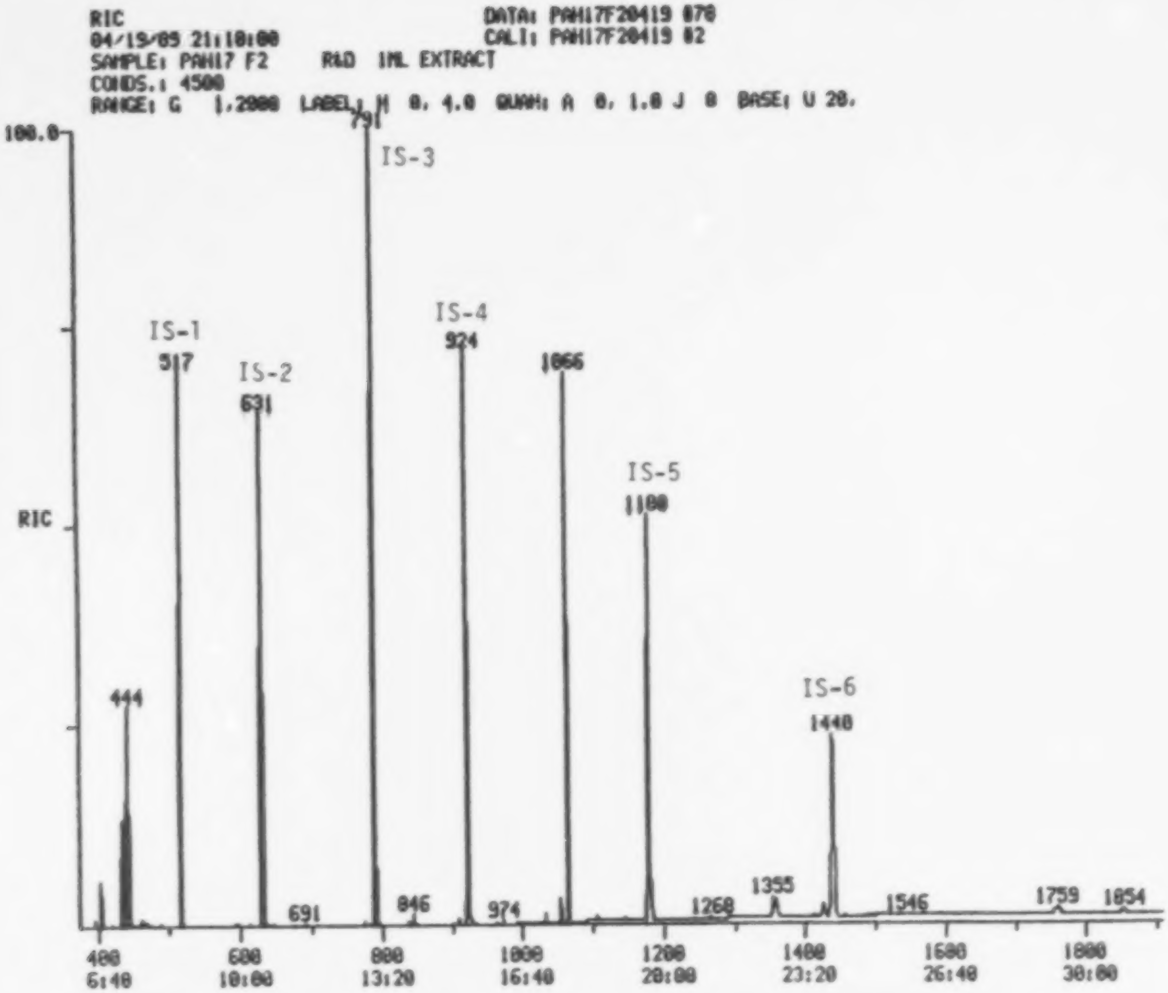


Figure 18. GC/MS chromatogram of extract of coal sample (NIST SRM 1632a) spiked with PAHs -- Fraction 2.

TABLE 20. COMPARISON OF RECOVERIES OBTAINED BY SFE WITH CERTIFIED VALUES REPORTED FOR SRS 103-100

Compound	Certified value (μg/g)	Value obtained by SFE[a] (μg/g)	Percent recovery
Naphthalene	32.4 ± 8.2	9.5	29.4
2-Methylnaphthalene	62.1 ± 11.5	37.6	60.5
Acenaphthylene	19.1 ± 4.4	5.3	27.7
Acenaphthene	632 ± 105	616	97.5
Dibenzofuran	307 ± 49	307	100
Fluorene	492 ± 78	209	42.4
Phenanthrene	1,618 ± 348	368	22.7
Anthracene	422 ± 49	177	41.9
Fluoranthene	1,280 ± 220	584	45.6
Pyrene	1,033 ± 289	592	57.3
Benzo(a)anthracene	252 ± 38	245	97.2
Chrysene	297 ± 26	319	107
Benzo(b+k)fluoranthene	152 ± 22	135	88.8
Benzo(a)pyrene	97.2 ± 17.1	36.4	37.4
Pentachlorophenol	965 ± 374	443	45.9

[a] The values given represent the sum of concentrations found in 9 fractions (only 4 fractions showed detectable levels). The sample size was 6 g. The sample was extracted with carbon dioxide containing 10 percent methanol. Fraction 1 was extracted at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. Fraction 2 was extracted at 250 atm/70°C/30 min dynamic, Fraction 3 at 300 atm/70°C/30 min dynamic, and Fractions 4 through 9 at 350 atm/70°C/every 30 min (in dynamic mode).

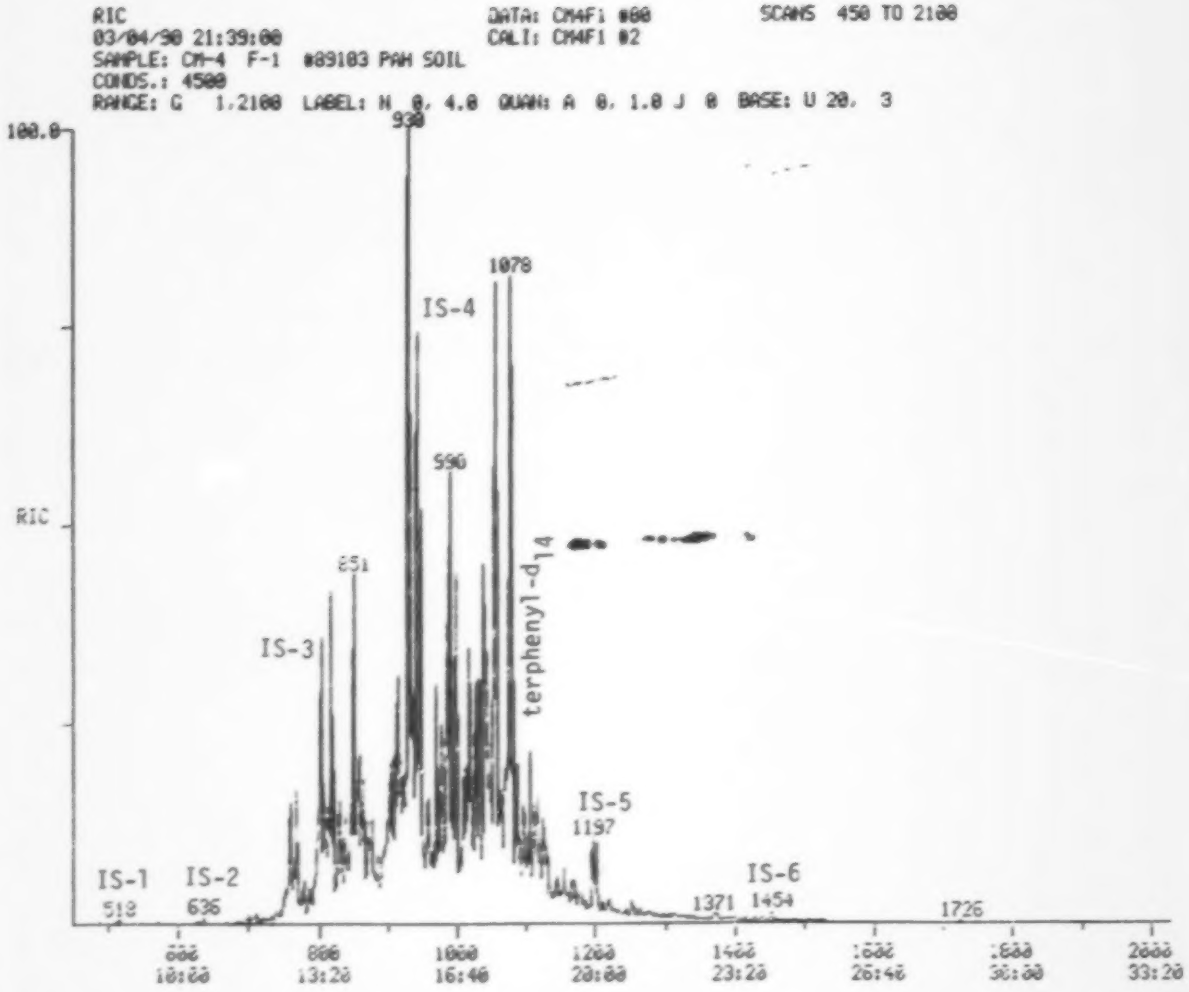


Figure 19. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 1.

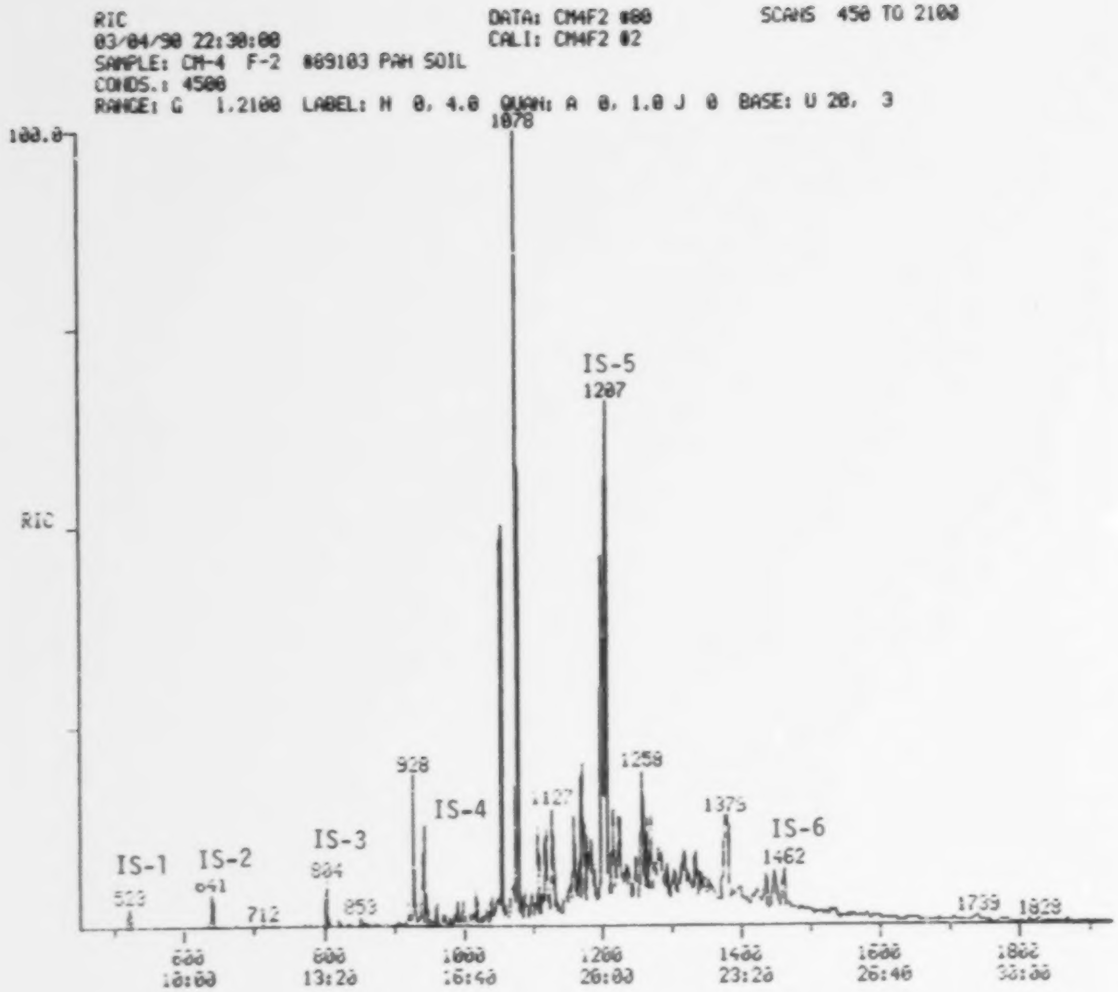


Figure 20. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 2.

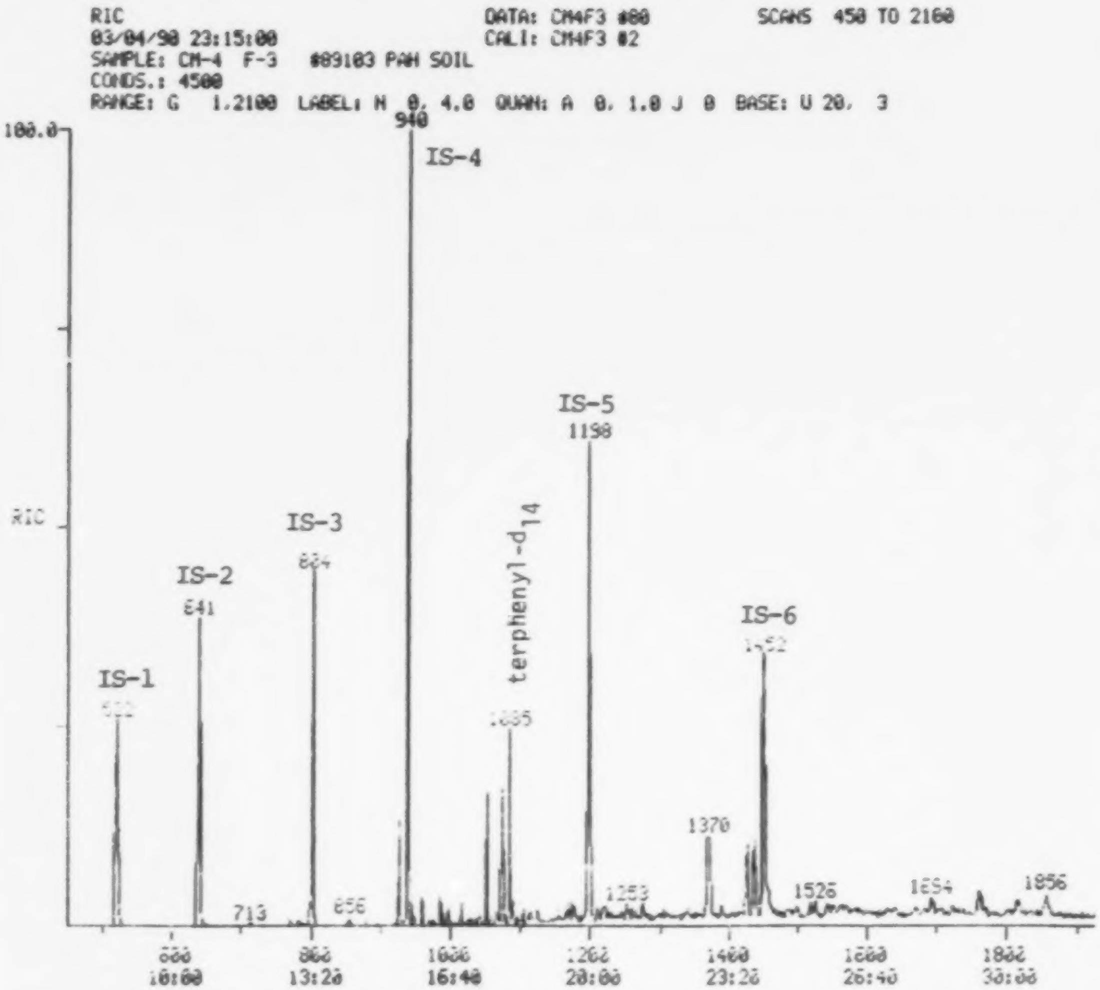


Figure 21. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 3.

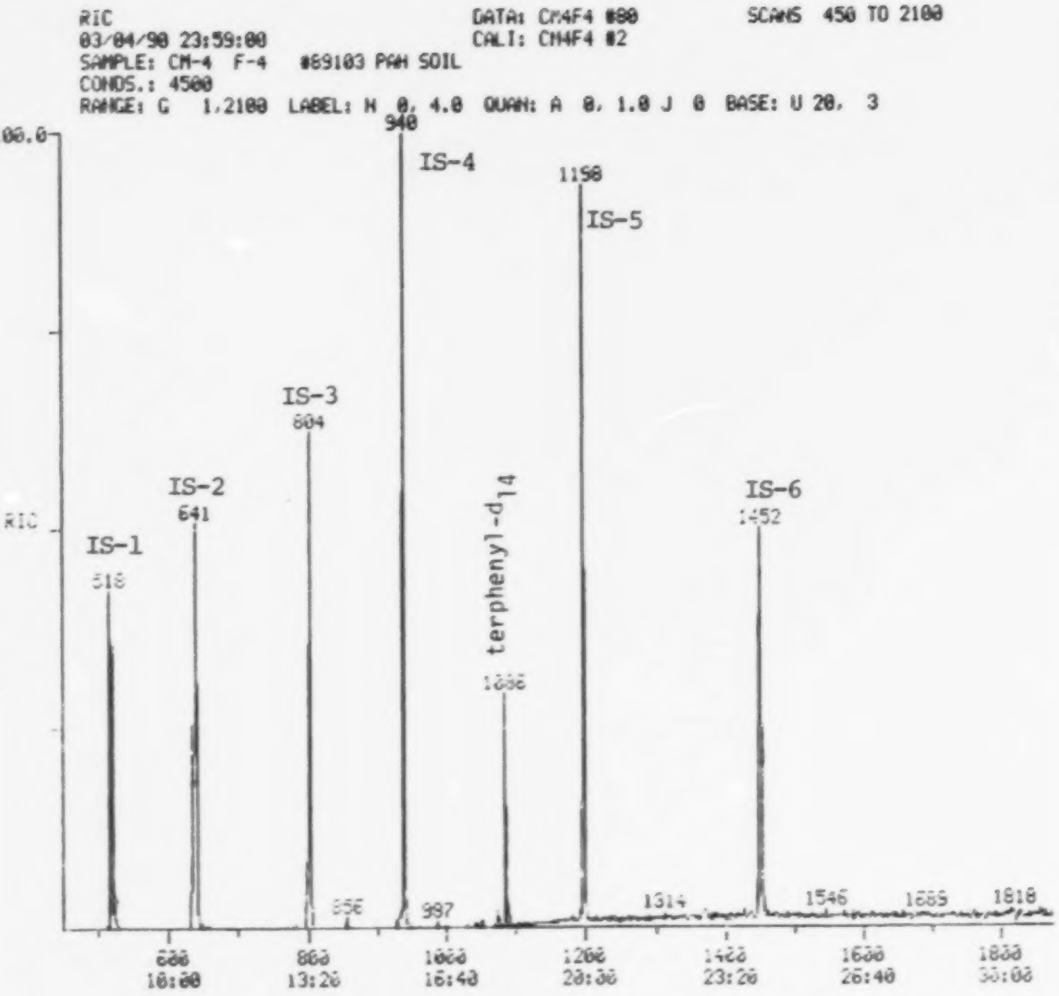


Figure 22. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 4.

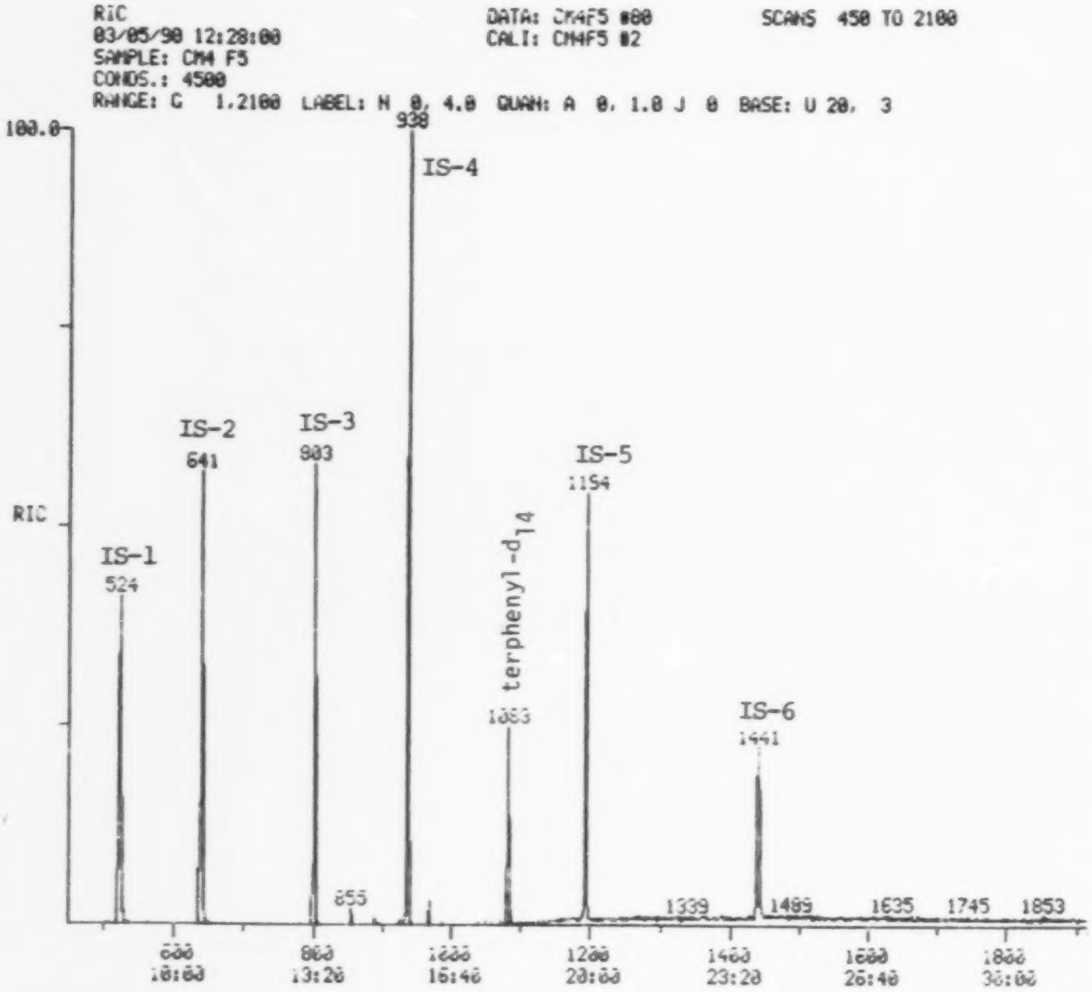


Figure 23. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 5.

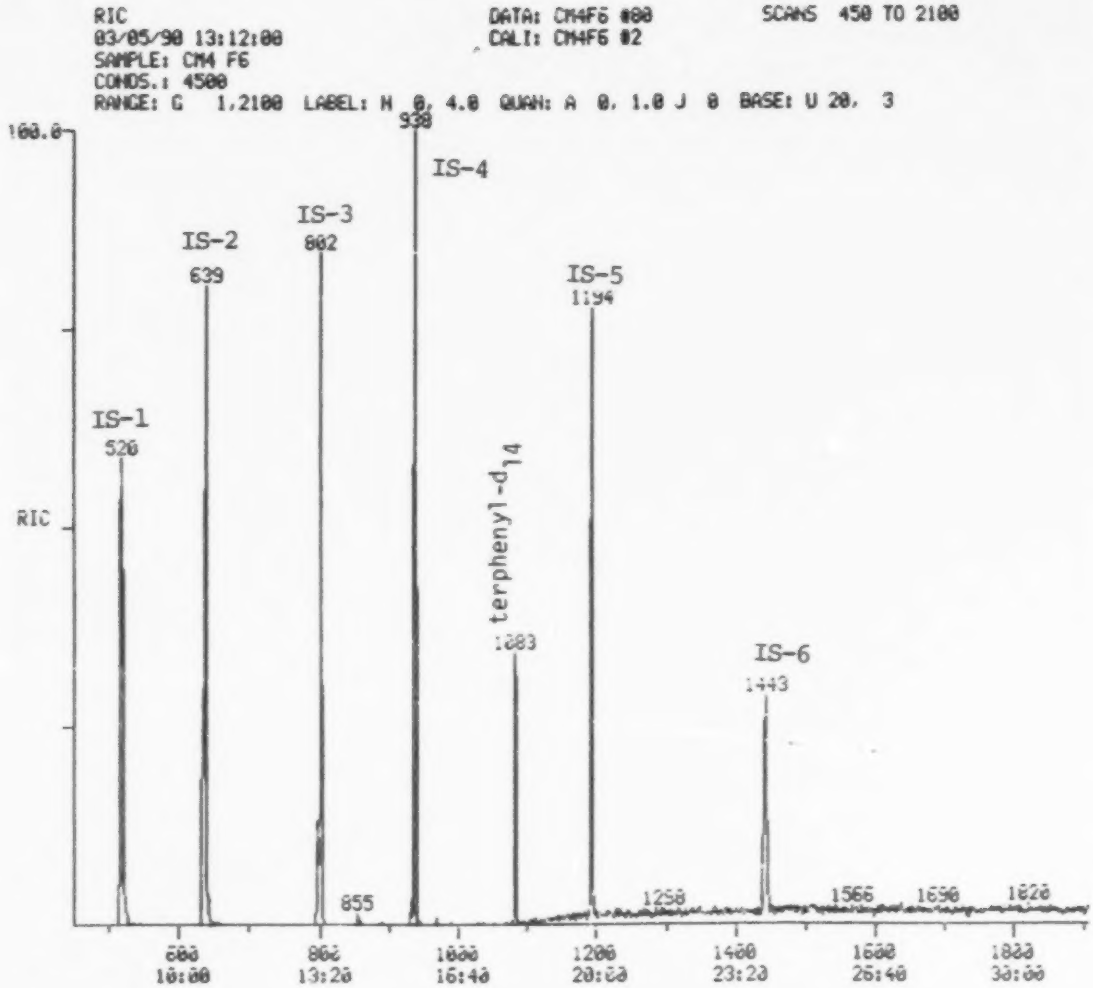


Figure 24. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 6.

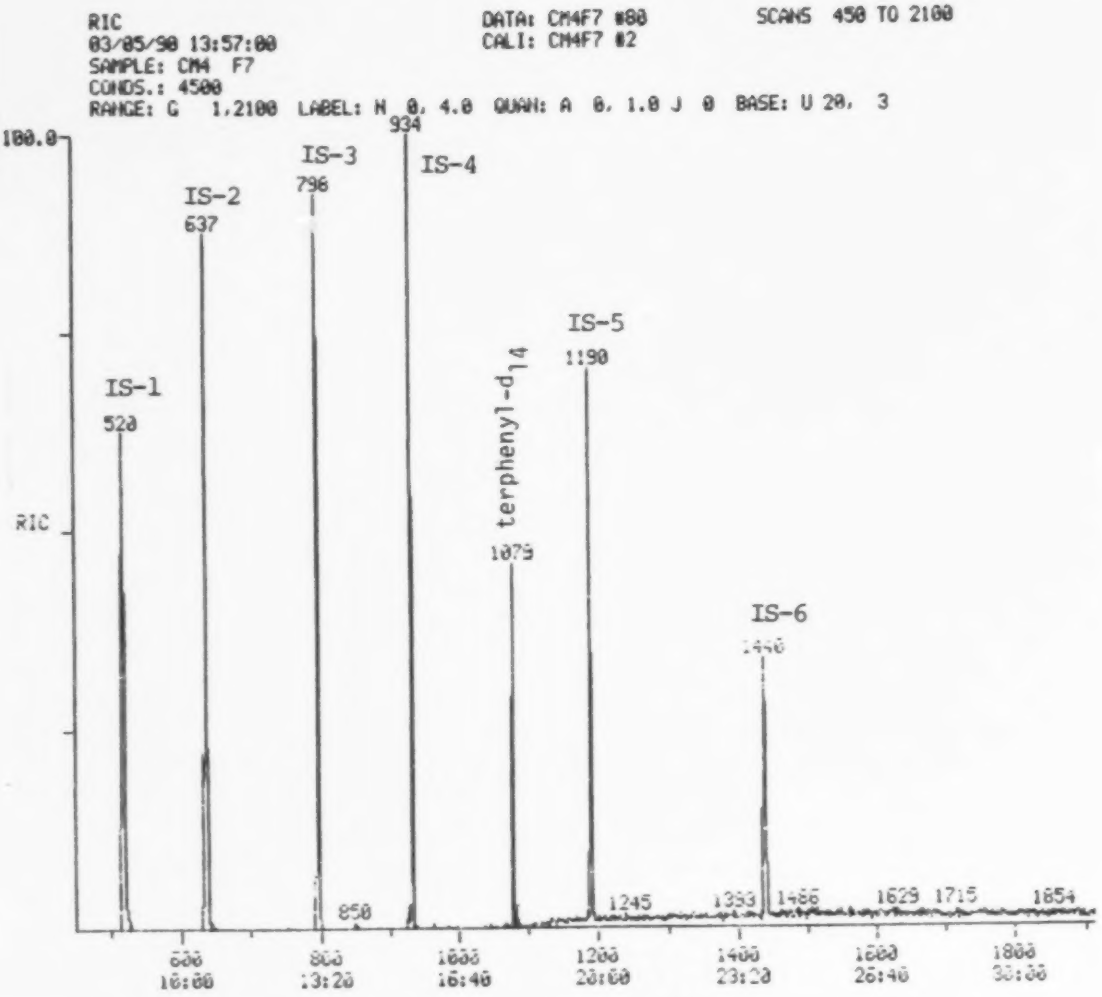


Figure 25. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 7.

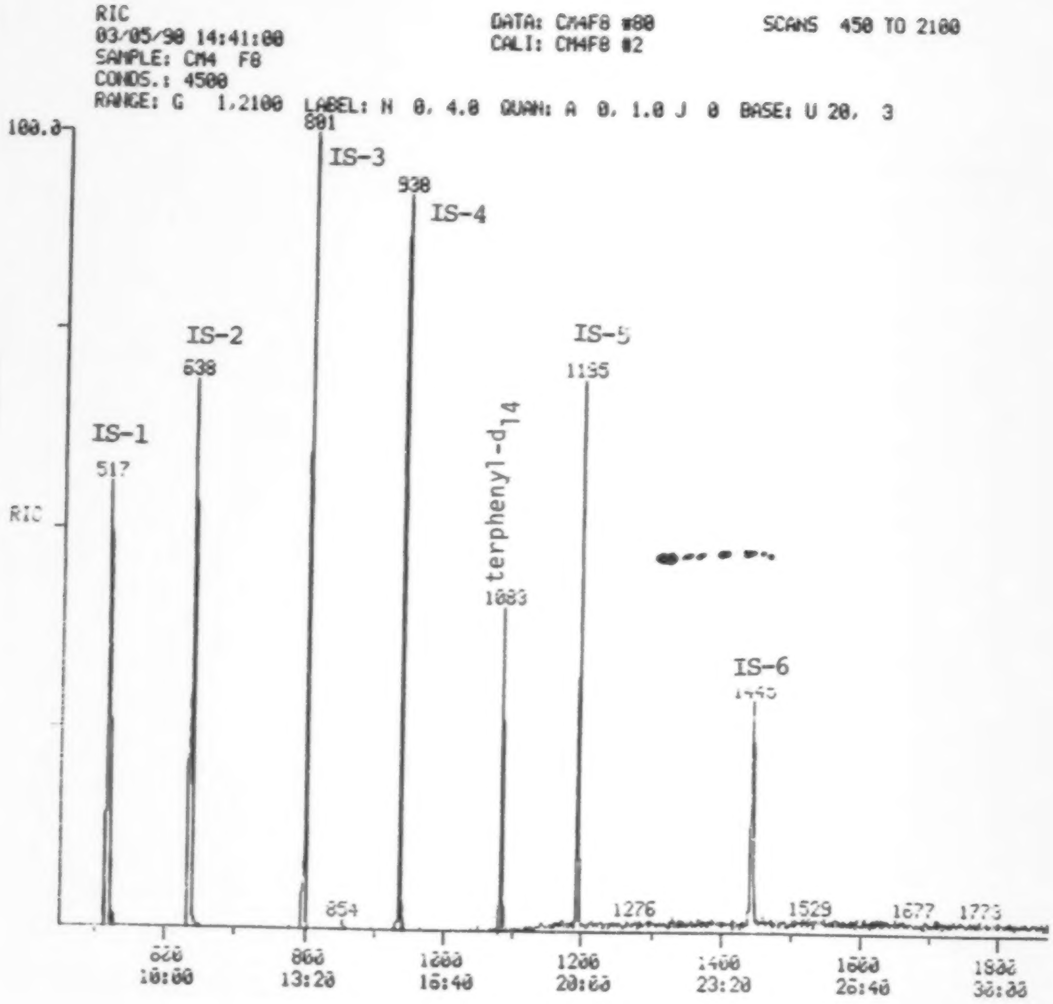
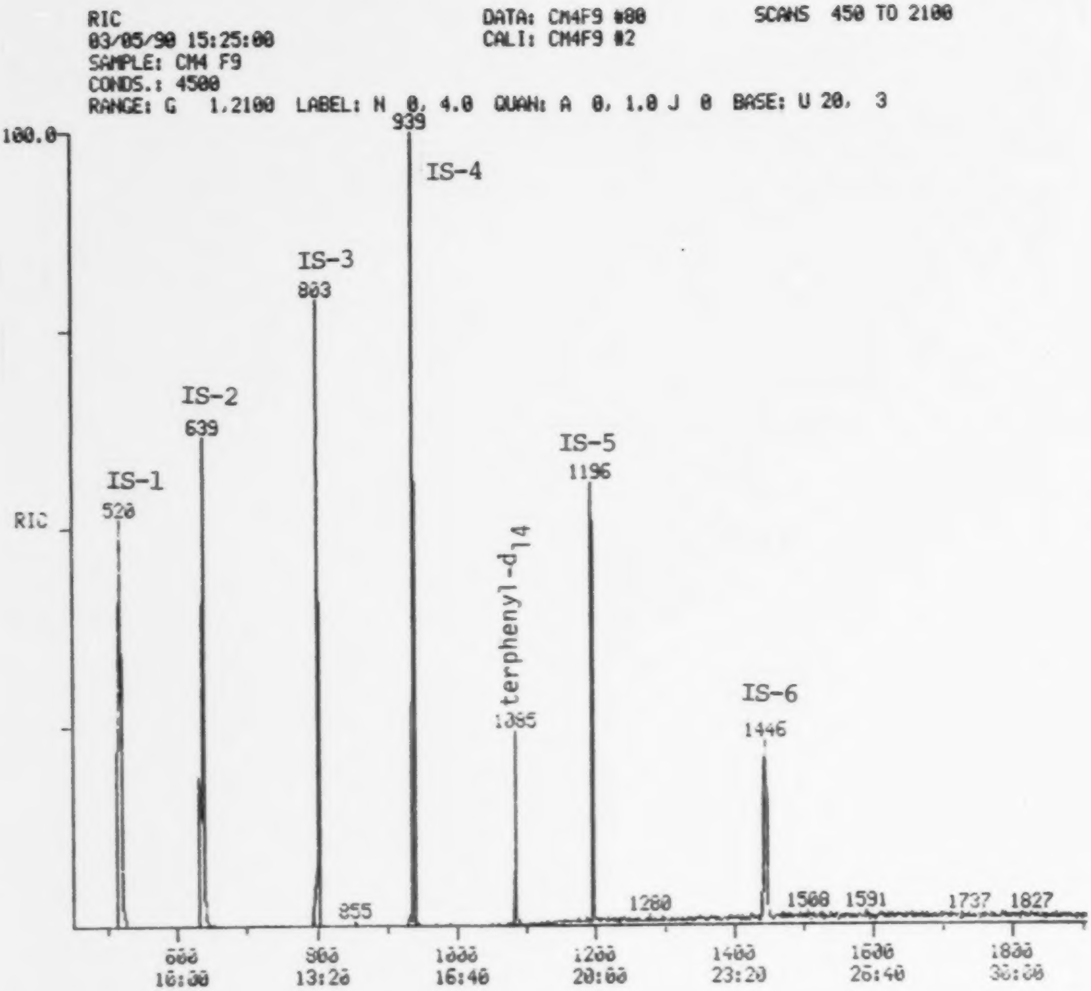


Figure 26. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 8.



```
RIC                                          DATA: CM4F9 #80          SCANS  450 TO 2100
03/05/90 15:25:00                            CALI: CM4F9 #2
SAMPLE: CM4 F9
CONDS.: 4500
RANGE: G   1,2100  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 27. GC/MS chromatogram of SRS 103-100 soil extract -- Fraction 9.

TABLE 21. COMPARISON OF RECOVERIES OBTAINED BY SFE WITH CERTIFIED VALUES REPORTED FOR SRS 103-100[a]

Compound	Certified value (μg/g)	Percent average recovery by SFE[b]	Percent RSD
Naphthalene	32.4 ± 8.2	63.8	11.1
2-Methylnaphthalene	62.1 ± 11.5	82.6	2.2
Acenaphthylene	19.1 ± 4.4	64.6	9.4
Acenaphthene	632 ± 105	98.2	4.2
Dibenzofuran	307 ± 49	92.9	3.5
Fluorene	492 ± 78	80.4	4.3
Phenanthrene	1,618 ± 348	124	9.8
Anthracene	422 ± 49	78.4	14.7
Fluoranthene	1,280 ± 220	92.3	6.5
Pyrene	1,033 ± 289	78.2	7.0
Benzo(a)anthracene	252 ± 38	67.6	4.2
Chrysene	297 ± 26	68.4	10.2
Benzo(b+k)fluoranthene	152 ± 22	53.3	14.3
Benzo(a)pyrene	97.2 ± 17.1	32.2	19.3
Pentachlorophenol	965 ± 374	141	11.1

[a] The number of determinations was three. The sample size was 2.5 g. Each extraction was performed with carbon dioxide at 300 atm and 70°C for 60 min; 10 percent moisture was added to each sample prior to extraction.

[b] As percent of certified values.

The second standard reference material extracted was a marine sediment identified as HS-3 and certified for 16 PAHs. The certified values and the values measured in the SFE extracts of SRM HS-3 are presented in Table 22. When carbon dioxide alone was used, most of the recoveries were below 50 percent (four were even below 20 percent). Use of modifier (10 percent methanol) improved the recoveries considerably: only four of the 16 recoveries were below 50 percent. Figures 28 through 32 show GC/MS chromatograms of each of the five fractions collected from the HS-3 marine sediment. Recoveries from the extraction of the HS-3 marine sediment at 350 atm/60°C/20 min with supercritical carbon dioxide are presented in Table 23 and in Figure 33.

The third standard reference material extracted was the NIST SRM 1941, a marine sediment certified for 11 PAHs. When extracted with supercritical carbon dioxide at 350 atm/60°C for 20 min, the recoveries of five of the compounds were ranging from 12.8 to 64.8 percent while six other PAHs present in the sample could not be detected (Table 24). We experienced frequent restrictor plugging while extracting this sample because of the elemental sulfur present at high concentrations in the sample. This may explain the low recovery data in Table 24.

Additional work performed by us on a Hewlett Packard Model 7680A SFE system (the results were not included in this report) confirmed the results in Table 24. A GC/MS chromatogram of an SFE extract from SRM 1941 is shown in Figure 34.

Tables 25 and 26 present the concentrations of compounds detected in the ten creosote-contaminated soil samples received from EPA-Las Vegas. These samples were extracted with supercritical carbon dioxide and supercritical carbon dioxide modified with 10 percent methanol. In each case, we collected two fractions per sample. In addition, we extracted portions of the same samples by sonication with methylene chloride/acetone (1:1) (Table 27). Although the conclusions we can make based on these data may not be valid because we cannot assure the homogeneity of the matrix, it is evident that the SFE recoveries with carbon dioxide were lower than the SFE recoveries with carbon dioxide modified with 10 percent methanol, and that in both cases the SFE recoveries were much lower than the recoveries obtained by sonicating the samples with methylene chloride/acetone (1:1). There was still a lot of material being extracted by SFE from the samples after 30 min as indicated by the high concentrations of compounds in Fraction 2. The moisture content of these samples varied from 14.9 to 21 percent, and this may have contributed to the lower extraction efficiencies by SFE.

The surrogate recovery data presented in Tables 28 through 31 indicate that the surrogate compounds are recovered in Fraction 1; with very few exceptions they meet the currently acceptable limits established by EPA for the Contract Laboratory Program. The recoveries of terphenyl-d_{14} were so high in Fraction 2 because this compound was spiked into the collection vessel and not the sample. The terphenyl-d_{14} recoveries indicate that no losses occur during the depressurization of the carbon dioxide, however, this is true only for those compounds that have vapor pressures similar to or lower than that of terphenyl-d_{14}.

TABLE 22. COMPARISON OF RECOVERIES OBTAINED BY SFE WITH CERTIFIED VALUES REPORTED FOR SRM HS-3

Compound	Certified value (μg/g)	SFE with carbon dioxide[a]			SFE with carbon dioxide with 10% methanol[b]	
		Concentration (μg/g)		Percent recovery	Concentration (μg/g)	Percent recovery
Naphthalene	9.0 ± 0.7	2.2	1.9	22.8	4.5	50.0
2-Methylnaphthalene	c	0.67	0.67	–	1.3	–
Acenaphthylene	0.3 ± 0.1	0.13	0.09	36.7	0.25	83.3
Acenaphthene	4.5 ± 1.5	3.3	2.9	68.9	4.2	93.3
Dibenzofuran	c	6.7	6.1	–	5.1	–
Fluorene	13.6 ± 3.1	6.3	5.5	43.4	4.8	35.3
Phenanthrene	85 ± 20	49	44	54.7	52	61.2
Anthracene	13.4 ± 0.5	5.6	4.4	37.3	7.0	52.2
Fluoranthene	60 ± 9	34	29	52.5	45	75.0
Pyrene	39 ± 9	20	17	47.4	25	64.1
Benzo(a)anthracene	14.6 ± 2.0	6.4	5.3	40.1	10	68.5
Chrysene	14.1 ± 2.0	6.7	5.7	44.0	10	70.9
Benzo(b)fluoranthene	7.7 ± 1.2	2.5	2.3	31.2	5.2	67.5
Benzo(k)fluoranthene	2.8 ± 2.0	2.8	2.4	92.9	5.7	204
Benzo(a)pyrene	7.4 ± 3.6	1.3	0.84	14.5	3.7	50.0
Indeno(1,2,3-c,d)pyrene	5.4 ± 1.3	0.44	0.31	6.9	2.0	37.0
Dibenzo(a,h)anthracene	1.3 ± 0.5	0.18	<0.1	13.9	0.4	30.8
Benzo(g,h,i)perylene	5.0 ± 2.0	3.1	<0.1	6.2	1.4	28.0

[a] Extracted in duplicate at 400 atm/70°C/25 min. The sample size was 2.3 g.

[b] The values given represent the sum of concentrations found in 5 fractions (only 3 fractions showed detectable levels). The sample size was 6 g. The extraction conditions are identical to those given in Table 20, except that only five fractions were prepared.

[c] Not certified.

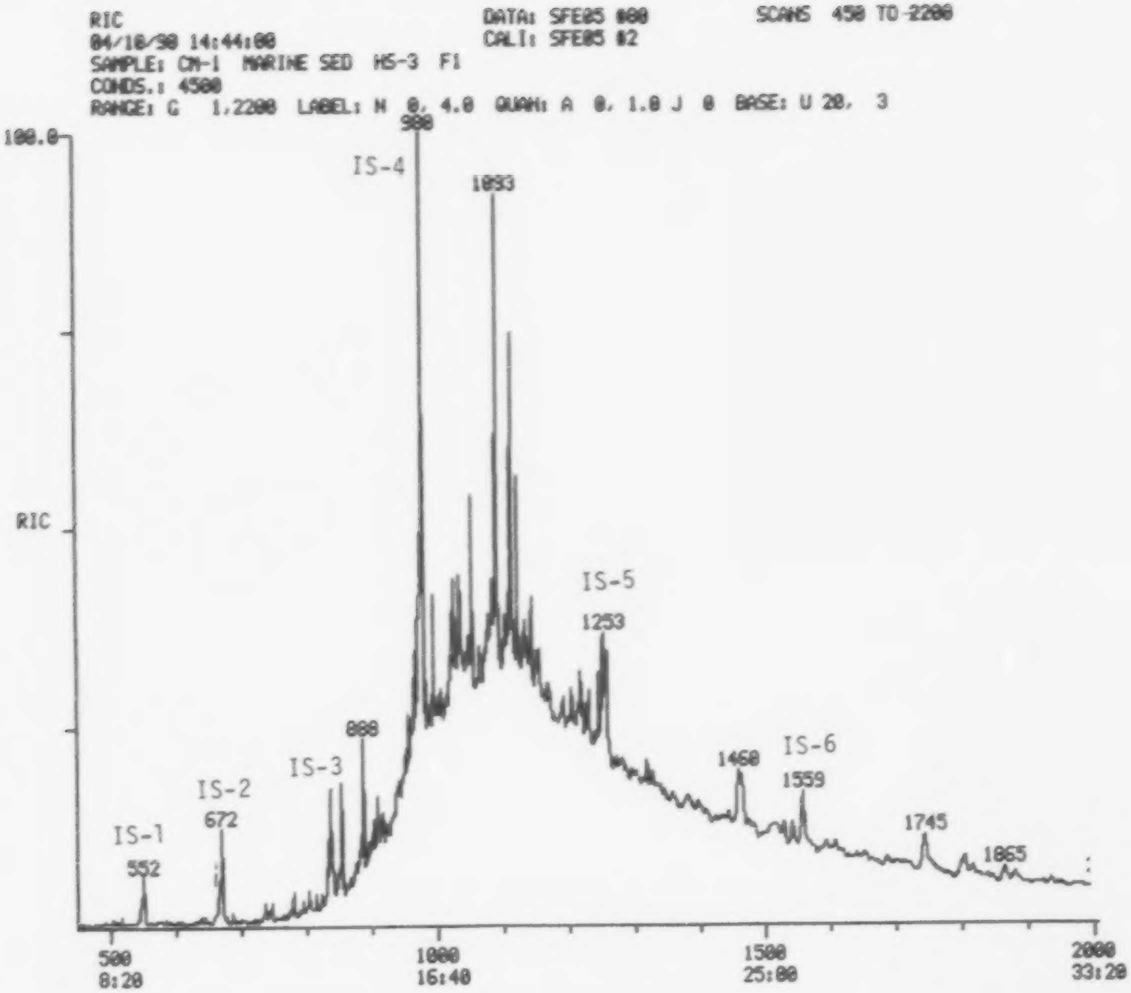


Figure 28. GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 1.

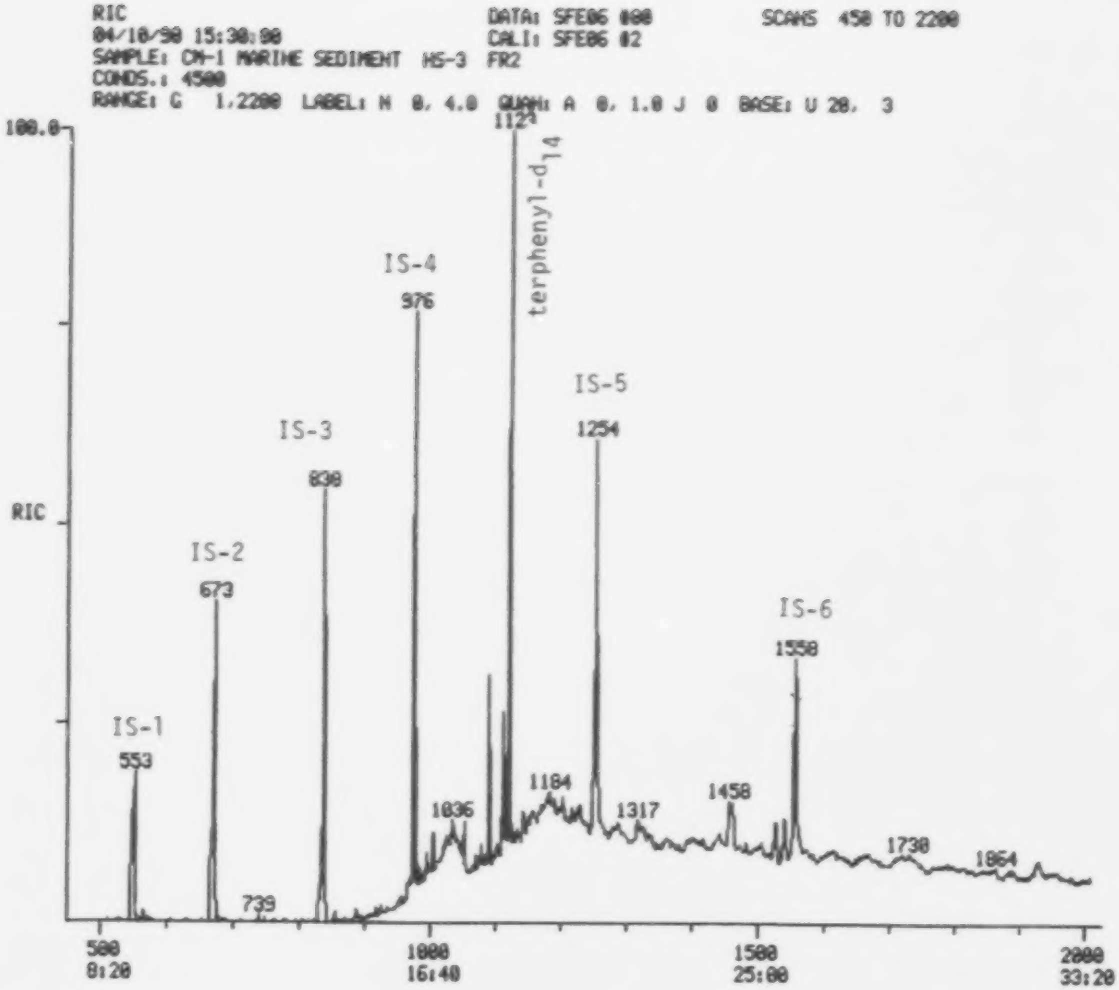


Figure 29. GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 2.

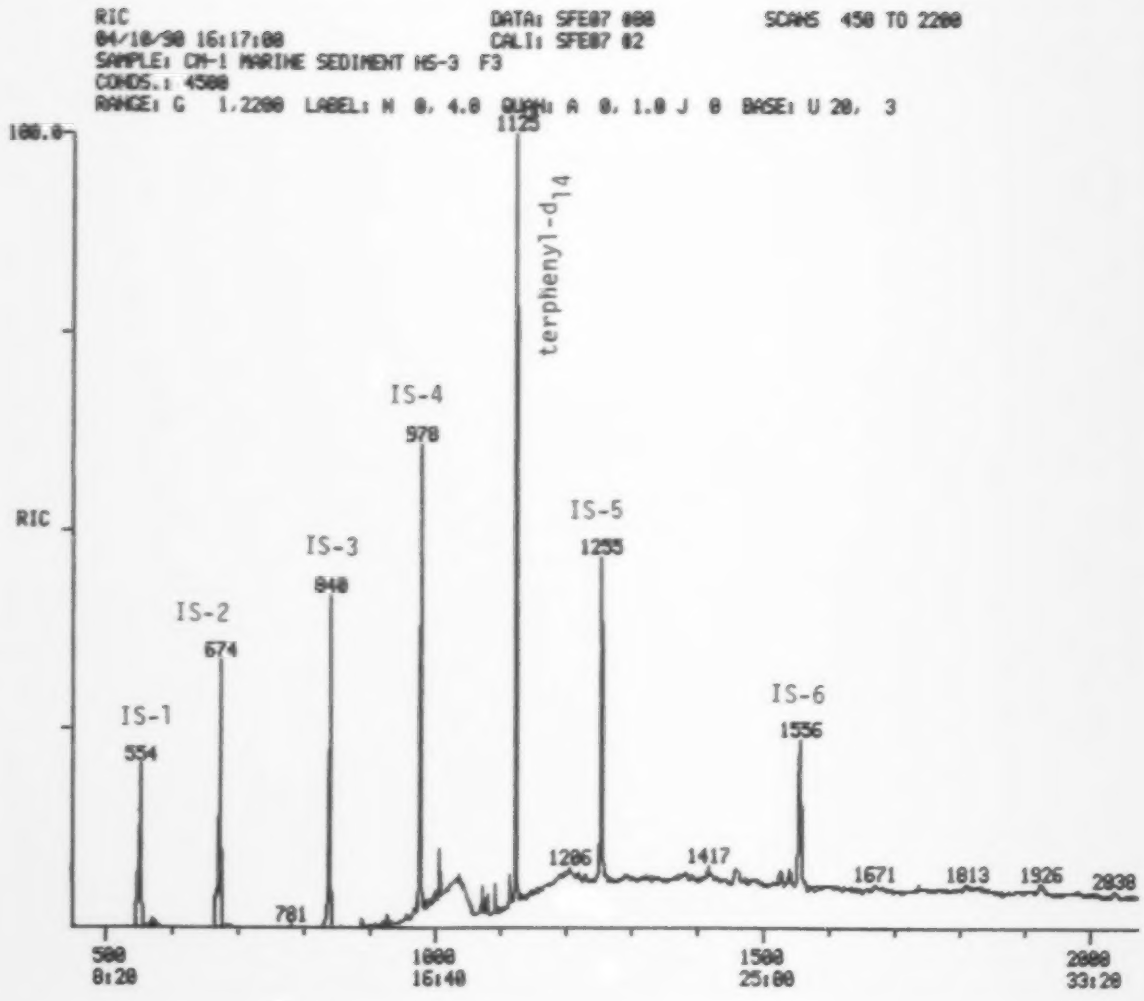


Figure 30. GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 3.

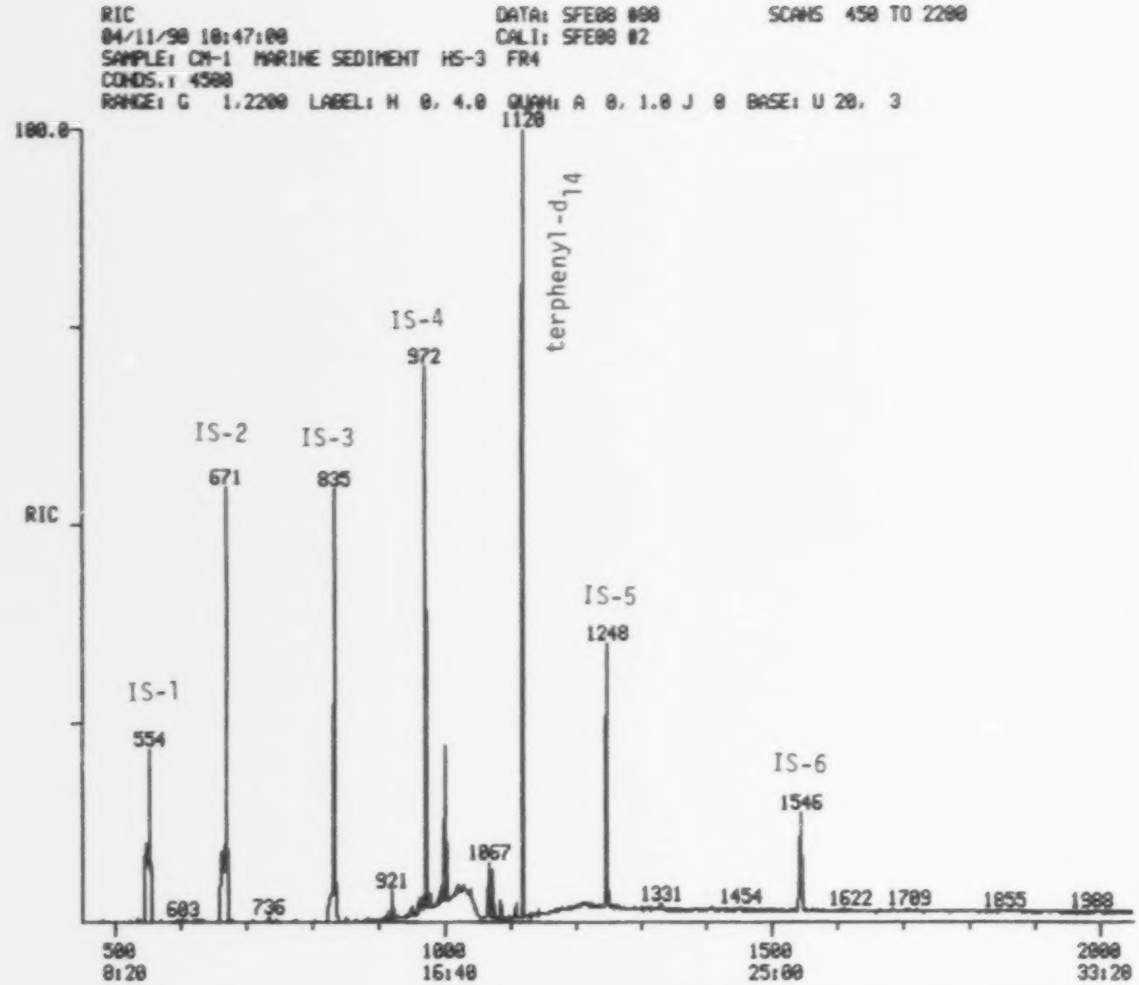
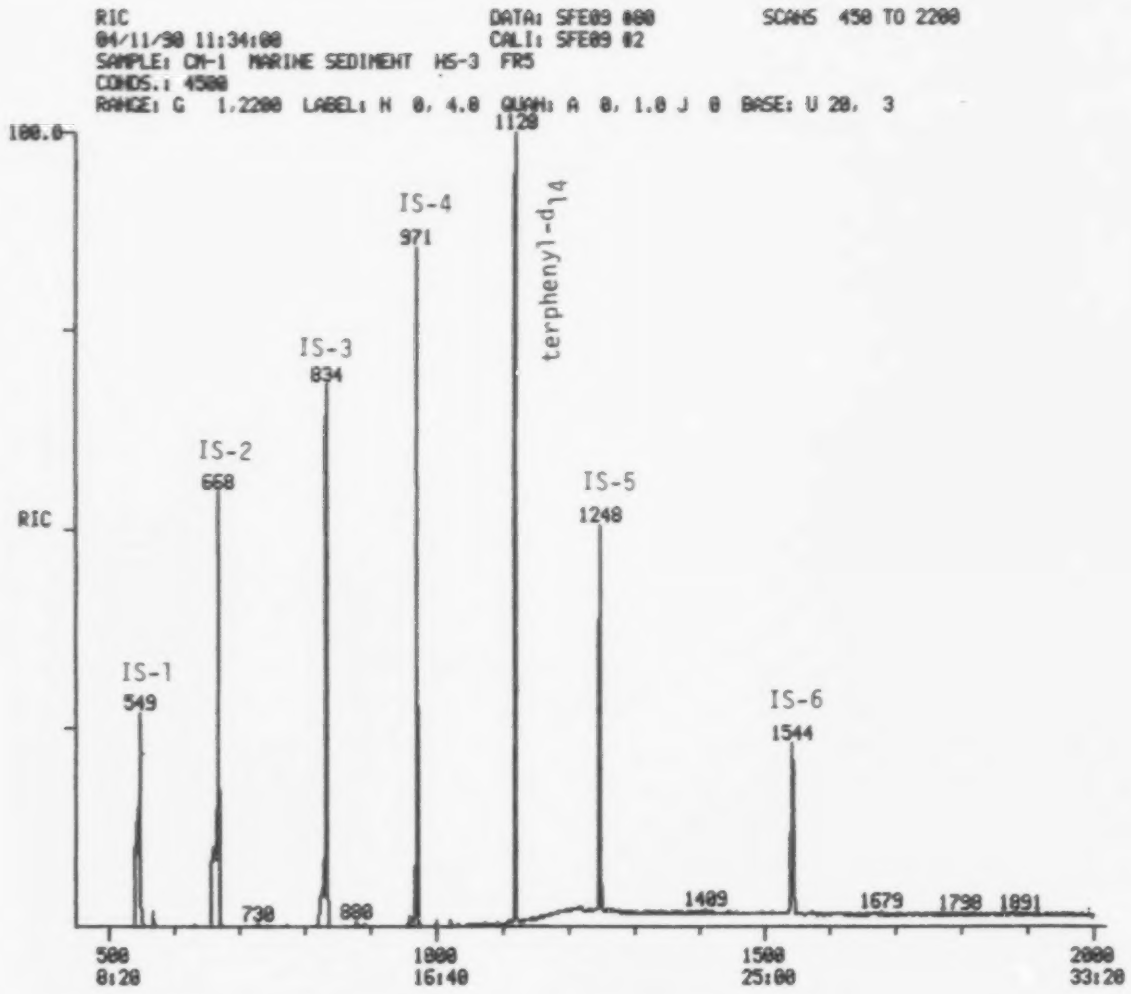


Figure 31. GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 4.



```
RIC                                           DATA: SFE09 #80         SCANS  450 TO 2200
04/11/90 11:34:00                             CALI: SFE09 #2
SAMPLE: CM-1  MARINE SEDIMENT  HS-3  FR5
CONDS.: 4500
RANGE: G   1,2200  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 32. GC/MS chromatogram of HS-3 marine sediment extract -- Fraction 5.

TABLE 23. COMPARISON OF RECOVERIES OBTAINED BY SFE WITH CERTIFIED VALUES REPORTED FOR SRM HS-3[a]

Compound	Certified value (µg/g)	Concentration found (µg/g)	Percent recovery
Naphthalene	9.00 ± 0.7	1.00	11.1
2-Methylnaphthalene	b	0.35	--
Acenaphthylene	0.3 ± 0.1	ND[c]	--
Acenaphthene	4.5 ± 1.5	0.85	18.9
Dibenzofuran	b	2.15	--
Fluorene	13.6 ± 3.1	2.05	15.1
Phenanthrene	85 ± 20	22.2	26.1
Anthracene	13.4 ± 0.5	1.65	12.3
Fluoranthene	60 ± 9	17.2	28.7
Pyrene	39 ± 9	10.8	27.7
Benzo(a)anthracene	14.6 ± 2.0	4.1	28.1
Chrysene	14.1 ± 2.0	4.3	30.5
Benzo(b)fluoranthene	7.7 ± 1.2	1.7	22.1
Benzo(k)fluoranthene	2.8 ± 2.0	2.4	85.7
Benzo(a)pyrene	7.4 ± 3.6	0.7	9.5
Indeno(1,2,3-c,d)pyrene	5.4 ± 1.3	ND	--
Dibenzo(a,h)anthracene	1.3 ± 0.5	ND	--
Benzo(g,h,i)perylene	5.0 ± 2.0	ND	--
Surrogate recovery			
2-Fluorophenol			49.6
Phenol-d_5			68.2
Nitrobenzene-d_5			48.7
2-Fluorobiphenyl			47.0
2,4,6-Tribromophenol			68.6

[a] The experiments were performed with supercritical carbon dioxide at 350 atm/60°C/20 min. The sample size was 2 g.

[b] Not certified.

[c] ND - not detected; estimated detection limit 0.1 µg/g.

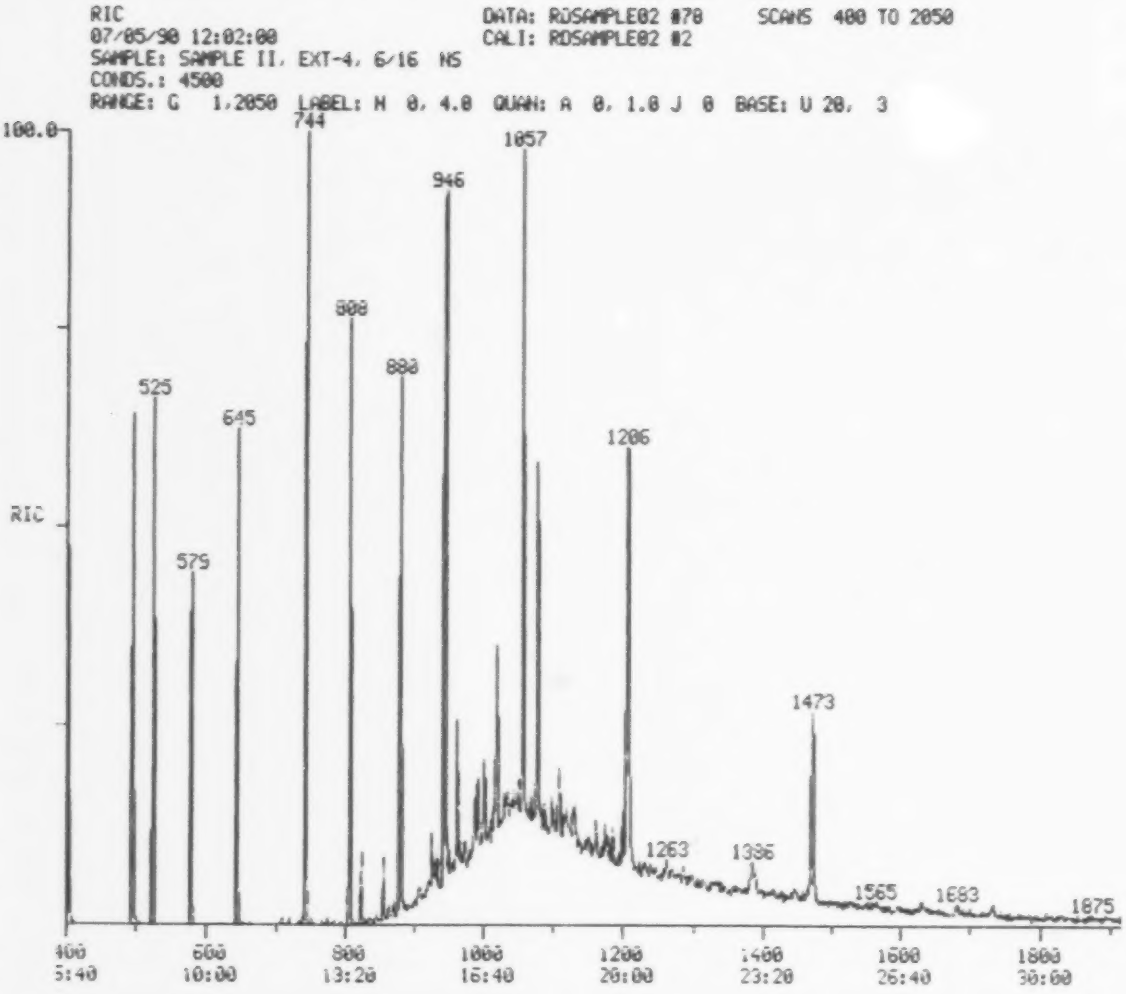


Figure 33. GC/MS chromatogram of HS-3 marine sediment extract.

TABLE 24. COMPARISON OF RECOVERIES OBTAINED BY SFE WITH CERTIFIED VALUES REPORTED FOR NIST SRM 1941[a]

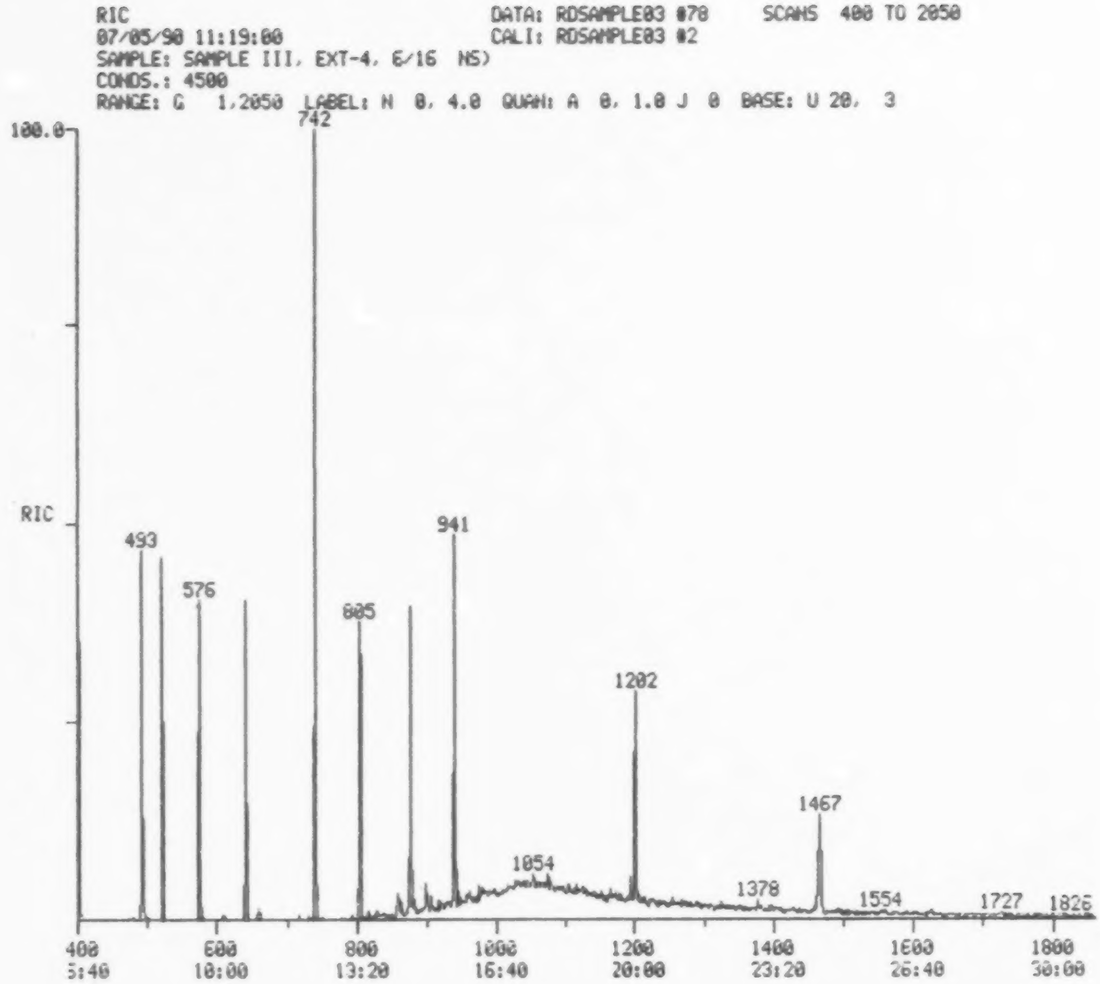
Compound	Certified value (μg/g)	Concentration found (μg/g)	Percent recovery
Phenanthrene	0.577 ± 0.059	0.25	43.3
Anthracene	0.202 ± 0.042	ND[b]	--
Pyrene	1.08 ± 0.20	0.70	64.8
Fluoranthene	1.22 ± 0.24	0.70	57.4
Benzo(a)anthracene	0.550 ± 0.079	0.20	36.4
Benzo(b)anthracene	0.78 ± 0.19	0.10	12.8
Benzo(k)anthracene	0.444 ± 0.049	ND	--
Benzo(a)pyrene	0.67 ± 0.13	ND	--
Perylene	0.422 ± 0.033	--	--
Benzo(g,h,i)perylene	0.516 ± 0.083	ND	--
Indeno(1,2,3-c,d)pyrene	0.569 ± 0.040	ND	--
Surrogate recovery			
2-Fluorophenol			64.1
Phenol-d_5			71.5
Nitrobenzene-d_5			86.1
2-Fluorobiphenyl			85.1
2,4,6-Tribromophenol			68.9

---

[a] The experiments were performed with supercritical carbon dioxide at 350 atm/60°C for 20 min. The sample size was 2 g.

[b] ND - not detected; estimated detection limit 0.1 μg/g.

Reproduced from
best available copy.



```
RIC                                        DATA: RDSAMPLE03 #78      SCANS  400 TO 2050
07/05/90 11:19:00                          CALI: RDSAMPLE03 #2
SAMPLE: SAMPLE III, EXT-4, 6/16  MS)
CONDS.: 4500
RANGE: G   1,2050  LABEL: N  0, 4.0  QUAN: A  0, 1.0 J  0  BASE: U 20,  3
```

Figure 34. GC/MS chromatogram of NIST SRM 1941 marine sediment extract.

TABLE 25. CONCENTRATIONS OF COMPOUNDS EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE FROM CREOSOTE-CONTAMINATED SOIL SAMPLES

	Concentration (μg/Kg)[a]									
	S-1B		S-2B		S-3B		S-4B		S-5B	
Compound	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2
Phenol	<300	<300	<300	<300	<300	<300	<300	<300	1,500	1,350
4-Methylphenol	<300	<300	<300	<300	<300	<300	<300	<300	4,650	3,090
Naphthalene	420	<300	17,940	2,340	192,090	1,170	31,560	2,100	161,880	133,530
2-Methylnaphthalene	<300	<300	12,480	1,710	147,420	<300	7,920	480	133,830	117,210
Acenaphthylene	<300	<300	660	3,210	4,110	<300	1,140	<300	6,330	4,410
Acenaphthene	2,280	<300	21,870	<300	141,270	450	37,650	4,980	165,840	119,670
Dibenzofuran	1,080	<300	12,570	1,830	86,580	<300	16,560	1,890	99,780	78,870
Fluorene	1,980	<300	17,970	2,880	110,790	<300	33,060	4,170	144,870	101,730
Phenanthrene	5,880	990	47,040	8,460	164,580	1,470	58,050	10,290	268,230	221,670
Anthracene	5,160	<300	13,350	3,030	63,570	<300	47,940	10,980	<300	<300
Fluoranthene	7,320	1,470	22,980	4,770	63,900	690	57,450	13,350	122,550	88,290
Pyrene	6,360	1,290	21,480	4,260	60,870	570	47,280	7,500	67,980	51,480
Benzo(a)anthracene	1,470	390	3,930	840	10,170	<300	12,180	1,890	19,290	12,480
Chrysene	2,190	570	3,960	<300	10,410	<300	13,260	2,130	17,070	11,070
Benzo(b)fluoranthene Benzo(k)fluoranthene	2,040	390	2,360	390	5,040	<300	7,950	960	5,940	6,480
Benzo(a)pyrene	870	<300	1,020	<300	2,250	<300	3,330	<300	4,140	2,730
Indeno(1,2,3-cd)pyrene	<300	<300	<300	<300	<300	<300	990	<300	<300	<300
Dibenzo(a,h)anthracene	<300	<300	<300	<300	<300	<300	420	<300	<300	<300
Benzo(g,h,i)perylene	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300

(continued)

[a] The values are reported on a wet-weight basis. Each sample (10 g) was spiked with 100 μL of 1 μg/μL surrogate componud solution (spiking level was 10 μg/g of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. Fraction 2 was collected by extraction with supercritical carbon dioxide at 250 atm/70°C/30 min dynamic

TABLE 25. (Concluded)

Compound	Concentration (μg/Kg)[a] S-6B Fraction 1	S-6B Fraction 2	S-7B Fraction 1	S-7B Fraction 2	S-8B Fraction 1	S-8B Fraction 2	S-9B Fraction 1	S-9B Fraction 2	S-10B Fraction 1	S-10B Fraction 2
Phenol	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
4-Methylphenol	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Napthalene	11,760	510	5,700	1,800	510	<300	2,250	630	775,110	239,550
2-Methylnaphthalene	6,090	480	3,030	1,440	480	<300	1,560	450	268,770	105,360
Acenaphthylene	780	<300	390	<300	<300	<300	<300	<300	7,830	3,510
Acenaphthene	15,960	2,370	8,430	2,160	2,100	<300	2,040	<300	223,470	127,290
Dibenzofuran	9,150	1,470	4,680	1,560	810	<300	2,460	690	136,950	80,130
Fluorene	22,890	4,050	330	2,250	1,290	<300	6,090	1,770	196,950	125,460
Phenanthrene	54,600	11,310	28,380	8,730	3,090	<300	11,580	3,360	288,450	172,170
Anthracene	48,960	13,380	27,240	<300	4,890	<300	70,500	21,810	79,980	164,100
Fluoranthene	68,730	17,010	45,030	3,870	20,280	<300	46,470	11,280	156,909	96,420
Pyrene	41,070	9,450	28,350	2,520	14,430	<300	34,020	9,120	78,510	52,620
Benzo(a)anthracene	10,530	2,400	6,420	660	2,820	<300	8,700	2,520	20,280	13,050
Chrysene	11,070	2,610	6,870	750	3,090	<300	13,170	4,380	17,610	12,230
Benzo(b)fluoranthene Benzo(k)fluoranthene	6,120	780	4,080	630	2,340	<300	3,870	2,130	3,960	3,270
Benzo(a)pyrene	2,790	540	1,830	<300	960	<300	1,980	660	2,610	2,070
Indeno(1,2,3-cd)pyrene	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Dibenz(a,h)anthracene	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Benzo(g,h,i)perylene	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300

[a] The values are reported on a wet-weight basis. Each sample (10 g) was spiked with 100 μL of 1 μg/μL surrogate compound solution (spiking level was 10 μg/g of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. Fraction 2 was collected by extraction with supercritical carbon dioxide at 250 atm/70°C/30 min dynamic.

TABLE 26. CONCENTRATIONS OF COMPOUNDS EXTRACTED FROM CREOSOTE-CONTAMINATED SOIL SAMPLES WITH SUPERCRITICAL CARBON DIOXIDE CONTAINING 10 PERCENT METHANOL

	Concentration ($\mu g/Kg$)[a]									
	S-1B		S-2B		S-3B		S-4B		S-5B	
Compound	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2
Phenol	<500	<500	<500	<500	<500	<500	<500	<500	2,050	1,450
Naphthalene	3,100	1,950	35,410	23,860	154,450	197,350	6,950	2,100	201,900	194,250
2-Methylnaphthalene	2,550	1,250	25,060	13,960	139,950	184,950	5,750	1,600	144,750	143,200
Acenaphthylene	550	<500	950	550	5,900	4,450	1,450	<500	8,550	7,700
Acenaphthene	8,650	3,950	38,720	20,910	158,650	177,150	51,300	14,250	190,050	188,550
Dibenzofuran	6,400	2,850	24,210	12,950	107,250	111,950	18,450	5,600	130,350	124,200
Fluorene	11,200	4,400	32,170	17,800	138,950	149,700	42,850	12,050	162,000	166,050
Phenanthrene	35,860	14,450	105,100	47,520	284,700	224,150	93,300	29,500	394,450	424,450
Anthracene	35,260	16,950	<500	14,400	<500	<500	91,600	25,950	<500	<500
Di-n-butylphthalate	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Fluoranthene	48,070	37,450	54,120	27,760	113,800	138,100	106,550	34,850	155,850	172,950
Pyrene	41,160	24,300	36,970	14,910	110,400	<500	91,700	24,650	148,150	151,550
Benzo(a)anthracene	11,450	9,450	6,950	3,700	22,450	18,600	20,150	4,250	37,650	54,300
Chrysene	13,450	12,900	<500	4,200	20,650	<500	<500	5,700	<500	<500
Benzo(b)fluoranthene	22,260	14,850	4,950	3,000	12,250	10,400	14,950	<500	11,850	18,950
Benzo(k)fluoranthene										
Benzo(a)pyrene	7,650	9,450	2,150	1,000	4,000	3,750	5,400	1,150	8,450	15,100
Indeno(1,2,3-cd)pyrene	2,500	<500	<500	<500	700	<500	1,450	<500	1,950	4,200
Dibenzo(a,h)anthracene	900	<500	<500	<500	<500	<500	<500	<500	750	1,950
Benzo(g,h,i)perylene	1,950	<500	<500	<500	<500	<500	<500	<500	1,500	3,350

(continued)

[a] The values are reported on a wet-weight basis. Each sample (10 g) was spiked with 100 μL of 1 $\mu g/\mu L$ surrogate compound solution (spiking level was 10 $\mu g/g$ of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. Fraction 2 was collected by extraction with supercritical carbon dioxide at 250 atm/70°C/30 min dynamic.

TABLE 26. (Concluded)

Compound	Concentration (μg/Kg)[a]									
	S-6B		S-7B		S-8B		S-9B		S-10B	
	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2	Fraction 1	Fraction 2
Phenol	<500	<500	<500	<500	<500	1,600	<500	<500	<500	<500
4-Methylphenol	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Naphthalene	4,900	850	12,950	14,400	700	<500	4,150	3,700	259,950	209,950
2-Methylnaphthalene	6,300	850	9,750	<500	550	<500	2,950	3,600	127,050	121,850
Acenaphthylene	1,250	<500	700	850	<500	<500	600	550	5,400	4,350
Acenaphthene	31,450	2,200	20,350	21,950	4,550	3,000	1,850	700	173,100	150,850
Dibenzofuran	22,850	2,400	13,950	15,900	1,550	550	4,100	4,750	123,750	111,550
Fluorene	56,650	7,300	19,800	24,150	3,200	1,100	9,750	12,450	145,450	165,300
Phenanthrene	141,200	32,600	52,300	143,800	9,950	4,050	21,300	<500	300,600	375,100
Anthracene	142,950	51,350	29,000	<500	13,450	4,900	<500	146,200	<500	<500
Di-n-butylphthalate	<500	2,100	<500	<500	<500	<500	4,700	<500	<500	<500
Fluoranthene	212,000	69,450	39,150	<500	72,650	29,250	85,200	60,700	80,350	<500
Pyrene	160,600	59,400	35,450	57,950	46,950	26,100	103,000	62,250	<500	<500
Benzo(a)anthracene	53,450	19,200	8,250	13,650	12,400	5,750	28,800	32,450	7,200	20,150
Chrysene	43,900	<500	<500	<500	14,550	8,600	<500	54,300	<500	<500
Benzo(b)fluoranthene Benzo(k)fluoranthene	19,700	13,600	10,350	19,050	8,750	9,100	36,050	41,100	18,000	9,350
Benzo(a)pyrene	12,950	9,250	3,700	7,200	5,950	3,400	13,450	22,950	1,300	3,950
Indeno(1,2,3-cd)pyrene	2,500	<500	<500	<500	1,300	<500	<500	5,150	<500	<500
Dibenzo(a,h)anthracene	850	<500	<500	<500	<500	<500	<500	2,300	<500	<500
Benzo(g,h,i)perylene	1,500	<500	<500	<500	<500	<500	<500	3,650	<500	<500

[a] The values are reported on a wet-weight basis. Each sample (10 g) was spiked with 100 μL of 1 μg/μL surrogate compound solution (spiking level was 10 μg/g of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. Fraction 2 was collected by extraction with supercritical carbon dioxide at 250 atm/70°C/30 min dynamic.

TABLE 27. CONCENTRATIONS OF COMPOUNDS EXTRACTED FROM CREOSOTE-CONTAMINATED SAMPLES BY SONICATION WITH METHYLENE CHLORIDE/ACETONE (1:1)

	Concentration (μg/Kg)[a]				
	S-1B	S-2B	S-3B	S-4B	S-5B
Phenol	NA[b]	<2,500	<2,500	<2,500	3,600
4-Methylphenol	NA	<2,500	<2,500	<2,500	10,270
Naphthalene	NA	153,470	711,070	68,000	1,104,400
2-Methylnaphthalene	NA	153,600	684,530	46,000	880,130
Acenaphthylene	NA	10,670	34,400	11,070	35,040
Acenaphthene	NA	236,930	492,130	207,470	463,330
Dibenzofuran	NA	174,530	434,530	102,930	410,530
Fluorene	NA	230,000	508,670	174,400	474,000
Phenanthrene	NA	510,270	1,083,870	412,530	987,600
Anthracene	NA	246,670	468,800	410,930	576,270
Fluoranthene	NA	540,270	925,730	632,670	623,600
Pyrene	NA	382,800	522,270	453,470	1,163,470
Benzo(a)anthracene	NA	133,470	265,600	173,470	301,600
Chrysene	NA	124,000	219,200	171,330	369,200
Benzo(b)fluoranthene	NA	94,530	162,530	120,670	240,670
Benzo(k)fluoranthene	NA	70,130	123,600	90,930	213,070
Benzo(a)pyrene	NA	69,470	124,270	88,130	191,470
Indeno(1,2,3-cd)pyrene	NA	34,400	55,070	42,270	39,870
Dibenzo(a,h)anthracene	NA	12,930	20,930	16,130	<2,500
Benzo(g,h,i)perylene	NA	28,800	52,670	44,930	27,870

[a] The values are reported on a wet-weight basis. Ten g sample was extracted with methylene chloride/acetone (1:1) according to Method 3550 in Reference 1. The extracts were subjected to GPC cleanup prior to GC/MS analysis.

[b] GC/MS analysis was not performed for this sample.

TABLE 27. (Concluded)

	Concentration (μg/Kg)[a]				
	S-6B	S-7B	S-8B	S-9B	S-10B
Phenol	<2,500	<2,500	<2,500	<2,500	<2,500
4-Methylphenol	<2,500	<2,500	<2,500	<2,500	<2,500
Naphthalene	93,870	15,070	2,270	6,670	3,273,070
2-Methylnaphthalene	32,800	20,130	1,730	7,070	1,149,600
Acenaphthylene	3,870	3,200	1,470	5,730	37,600
Acenaphthene	75,330	45,200	11,470	6,400	599,730
Dibenzofuran	48,000	34,530	4,670	14,130	544,530
Fluorene	89,730	50,530	8,530	34,800	686,000
Phenanthrene	233,470	135,600	28,530	81,870	1,474,670
Anthracene	215,070	108,270	50,400	333,200	628,000
Fluoranthene	227,200	164,130	182,930	236,800	1,097,470
Pyrene	468,930	133,070	256,270	204,800	573,270
Benzo(a)anthracene	95,470	40,270	54,800	96,800	292,270
Chrysene	122,800	50,800	68,670	162,670	293,870
Benzo(b)fluoranthene	89,870	56,800	72,400	132,270	192,800
Benzo(k)fluoranthene	76,270	40,130	52,400	99,730	119,330
Benzo(a)pyrene	69,600	39,870	47,070	94,930	146,530
Indeno(1,2,3-cd)pyrene	13,200	19,730	21,200	58,130	65,200
Dibenzo(a,h)anthracene	<2,500	6,000	3,870	18,530	24,800
Benzo(g,h,i)perylene	12,000	17,870	24,530	56,530	66,270

[a] The values are reported on a wet-weight basis. Ten g sample was extracted with methylene chloride/acetone (1:1) according to Method 3550 in Reference 1. The extracts were subjected to GPC cleanup prior to GC/MS analysis.

[b] GC/MS analysis was not performed for this sample.

TABLE 28. SURROGATE RECOVERIES IN FRACTION 1 (SUPERCRITICAL CARBON DIOXIDE)[a]

Sample	SU-1 2-Fluoro-phenol	SU-2 Phenol -d_5	SU-3 Nitrobenzene -d_5	SU-4 2-Fluoro-biphenyl	SU-5 2,4,6,-Tribromo-phenol	SU-6 Terphenyl -d_{14}[c]
S-1B	82.3	74.6	80.3	71.5	59.2	96.4
S-2B	51.6	58.5	45.9	41.9	45.0	97.7
S-3B	78.7	86.7	70.1	86.1	73.5	95.8
S-4B	95.4	78.1	84.1	100.0	70.6	103.0
S-5B	63.1	59.6	54.6	67.8	14.7	86.5
S-6B	78.6	90.7	70.8	67.0	78.6	96.4
S-7B	86.5	88.3	93.2	82.8	97.5	99.7
S-8B	90.6	89.1	102.7	89.5	100.8	92.4
S-9B	79.0	12.6	84.9	87.5	33.7	85.8
S-10B	66.5	66.0	93.3	60.2	41.8	80.3
QC-limits[b]	21-100	10-94	35-114	43-116	10-123	33-141

[a] Each sample (10 g) was spiked with 100 µL of 1 µg/µL surrogate compound solution (spiking level was 10 µg/g of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic.

[b] The QC limits established by EPA for the Contract Laboratory Program.

[c] Terphenyl-d_{14} was not spiked with the other surrogates onto the sample, but it was spiked in the collection vial (internal standard for SFE).

TABLE 29. SURROGATE RECOVERIES IN FRACTION 2 (SUPERCRITICAL CARBON DIOXIDE)[a]

Sample	SU-1 2-Fluoro-phenol	SU-2 Phenol -d_5	SU-3 Nitrobenzene -d_5	SU-4 2-Fluoro-biphenyl	SU-5 2,4,6,-Tribromo-phenol	SU-6 Terphenyl -d_{14}
S-1B	ND	ND	ND[b]	ND	ND	101.0
S-2B	3.1	ND	ND	ND	ND	98.3
S-3B	ND	ND	ND	ND	ND	93.7
S-4B	ND	ND	ND	ND	ND	104.0
S-5B	17.0	18.8	11.8	11.3	ND	83.3
S-6B	3.6	ND	ND	ND	ND	98.7
S-7B	4.7	6.5	4.8	5.6	ND	104.0
S-8B	ND	ND	ND	ND	ND	106.0
S-9B	3.5	20.3	ND	ND	13.4	86.8
S-10B	12.5	16.3	10.8	11.2	ND	89.5

[a] In this case only terphenyl-d_{14} was spiked into the collection vial. Fraction 2 was collected by extraction with supercritical carbon dioxide at 250 atm/70°C/30 min dynamic.

[b] Not detected.

TABLE 30. SURROGATE RECOVERIES IN FRACTION 1 (SUPERCRITICAL CARBON DIOXIDE WITH 10 PERCENT METHANOL)[a]

Sample	SU-1 2-Fluoro-phenol	SU-2 Phenol -d_5	SU-3 Nitrobenzene -d_5	SU-4 2-Fluoro-biphenyl	SU-5 2,4,6,-Tribromo-phenol	SU-6 Terphenyl -d_{14}[c]
S-1B	59.9	31.9	70.0	68.9	47.0	81.9
S-2B	46.4	31.5	66.5	77.2	51.9	74.5
S-3B	62.7	46.8	63.6	73.0	48.2	72.6
S-4B	29.4	16.6	30.4	36.5	29.8	78.0
S-5B	0	17.5	17.0	20.2	12.6	81.9
S-6B	86.7	74.9	82.1	93.5	98.8	93.4
S-7B	73.9	63.5	89.3	89.7	74.3	76.4
S-8B	118	110	102	112	129	79.5
S-9B	80.9	68.9	82.1	88.5	76.3	76.8
S-10B	56.1	36.2	55.4	75.1	38.5	81.8
QC limits[b]	21-100	10-94	35-114	43-116	10-123	33-141

[a] Each sample (10 g) was spiked with 100 µL of 1 µg/µL surrogate compound solution (spiking level was 10 µg/g of wet soil). Fraction 1 was collected by extraction with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic.

[b] The QC limits established by EPA for the Contract Laboratory Program.

[c] Terphenyl-d_{14} was not spiked with the other surrogates onto the sample, but it was spiked in the collection vial (internal standard for SFE).

TABLE 31. SURROGATE RECOVERIES IN FRACTION 2 (SUPERCRITICAL CARBON DIOXIDE WITH 10 PERCENT METHANOL)[a]

Sample	SU-1 2-Fluorophenol	SU-2 Phenol -d_5	SU-3 Nitrobenzene -d_5	SU-4 2-Fluorobiphenyl	SU-5 2,4,6,-Tribromophenol	SU-6 Terphenyl -d_{14}
S-1B	12.3	12.7	5.9	7.9	20.3	100.0
S-2B	1.9	ND	4.0	4.2	2.0	92.3
S-3B	4.4	4.0	7.0	6.5	7.3	83.4
S-4B	12.3	4.8	28.1	33.4	15.7	83.8
S-5B	7.4	7.1	4.6	4.0	5.6	79.9
S-6B	3.0	2.3	ND	2.6	8.4	84.6
S-7B	ND[b]	ND	ND	ND	ND	ND
S-8B	ND	2.1	ND	2.4	8.0	93.8
S-9B	3.0	ND	ND	ND	6.8	94.6
S-10B	ND	12.4	7.7	7.0	5.8	80.7

[a] In this case only terphenyl-d_{14} was spiked into the collection vial. Fraction 2 was collected by extraction with supercritical carbon dioxide with 10 percent methanol at 250 atm/70°C/30 min dynamic.

[b] Not detected.

5.1.6 Summary of the SFE Preliminary Work

As can be seen from the above discussion of the experimental results, the extraction efficiencies we achieved with a variety of samples varied considerably. Some of our recoveries were much lower than those published by others. However, on closer evaluation, it turns out that many of the studies reported so far in the literature were more of a qualitative nature, were often conducted with homemade equipment, focused mostly on PAHs, and used small sample sizes (as small as a few milligrams). To develop an SFE method that can successfully be applied to samples of interest to the EPA, we have to use commercially available equipment, consider a wide variety of sample matrices and groups of pollutants, and use sample sizes large enough to compensate for the inevitable inhomogeneities of most real environmental and hazardous waste samples. We, therefore, decided to reassess our approach to SFE evaluation and first look more closely at the many variables that affect SFE efficiency.

Sample Size

Small sample sizes (as small as 20 mg or even less) are adequate when homogeneous material is extracted, e.g., for the extraction of stabilizers and plasticizers from polymers, extraction of waxes, many pharmaceutical materials, etc. However, most environmental and waste samples are inhomogeneous even after mixing. Therefore, the sample sizes specified in SW-846 are 10 g (Soxhlet) and 30 g or 2 g (sonication), depending on the concentrations of the analytes in the sample. For this reason, samples for SFE in the environmental field should be in the 1- to 10-g range, preferably at least 5 g.

Recoveries

There is a lack of standard reference materials that cover the matrices and pollutants of environmental concern. The materials that are available were certified for only a very limited number of compounds, e.g., PAHs. It is therefore difficult, even currently impossible, to determine absolute extraction efficiencies for most analytes because in most cases, removal of a spike from a sample matrix is much easier than removal of "incorporated" or "native" compounds. This, however, is a problem that hampers the evaluation of all extraction methods, not just SFE, and one is usually confined to comparing relative extraction efficiencies.

Temperature and Pressure Manipulation

Temperature and pressure changes affect the density and viscosity of a SF and therefore its solubilizing ability. However, little is understood about what happens on the surfaces of the solid matrices during the extraction process, and what the desorption, solvation, and transport mechanisms are, and little is known about how to optimize p and T for specific matrices and analyte groups. Just raising the pressure does not seem to be the answer.

Static or Dynamic Extraction?

An understanding of the desorption and transport mechanisms of a solute under supercritical conditions would provide clues if the use of static or dynamic extraction conditions, or a combination of the two, would be advantageous; whether rapid pressure fluctuations would improve extraction rates and, maybe, extraction efficiencies and selectivities; and whether application of ultrasound could enhance extraction efficiency and rate, as has been suggested (8).

Modifiers

Modifiers are liquids that can be added to the SF or directly to the sample. They usually are more polar than the basic SF; for example, benzene, toluene, methanol, and acetone have been added to carbon dioxide. Their use improves solvent strength and affects selectivity. However, we are mostly confined to the trial-and-error approach. We do not know to what extent, and in what way, the modifier changes the properties of the supercritical system and in which way solubility is enhanced, and the selection of modifiers for specific applications is still largely guesswork.

Based on our results from the extraction of relatively simple matrices, we developed a draft protocol in the SW 846 format, "Extraction Procedure Using Supercritical Fluids" (Appendix B). Our goal was to write a generic protocol that is applicable to as many different SFE systems as possible. This protocol was written for solid matrices like soils, sediments, etc.; the target analytes include organochlorine pesticides, organophosphorus pesticides, nitroaromatics, haloethers, base/neutral/acidic compounds, and PAHs. The protocol addresses interferences, apparatus and materials, sample preparation (including extraction), and quality assurance. The protocol will be refined and updated as additional data become available.

5.2 METHOD OPTIMIZATION

The experimental conditions of our method optimization study focused on two sets of seven variables listed in Tables 1 and 2, each chosen at two levels. A full factorial design would have required 128 experiments. Instead, this design allowed us to perform only eight experiments, and to estimate the main effects of the two sets of seven variables; however, we could not test for statistical significance of any of these effects because there were no degrees of freedom for the error terms. Tables 32 and 33 summarize the recovery data for the eight experiments performed for each test using SRS 103-100. From these tables, one can calculate the effect on the recovery of each variable at its low and its high value using Equations 1 through 7 (page 14 of this report). To get an overall picture of which variables affect the recovery of the highest number of compounds, the group differences (Tables 34 and 35) were ranked and the ranks across the 15 compounds were summed up in Tables 36 through 38.

From these sums, we concluded that in Test 1 the recovery was most affected by time (sum of ranks 88) and least affected by the volume of the modifier (sum of ranks 31). Pressure and moisture ranked second (sum of ranks 70) and third (sum of ranks 69) in importance after time. The sum of ranks for sample size, temperature, and cell volume are 65, 50, and 47, respectively. Figures 35 through 42 show the relative change in recovery for each compound numbered as in Table 32 and for each of the seven variables.

When the experiments were performed at the same pressure, temperature, and moisture conditions but toluene was used as modifier and the extraction vessel was pressurized for 15 or 30 min during the 60-min extraction, then recovery (Table 39) was most affected by moisture (sum of ranks 88) followed by pressure (sum of ranks 70) and volume of toluene (sum of ranks 58). The fourth variable to influence was the static extraction time (sum of ranks 57). Temperature, volume of collection solvent, and the presence/absence of glass beads were the least important. Figures 43 through 50 show the relative changes in recovery for each compound and for each of the seven variables investigated in Test 2. The group differences for Test 2 were ranked and the ranks across the 15 compounds were summed up in Tables 40 and 41.

TABLE 32. EXTRACTION OF SRS 103-100 WITH SUPERCRITICAL CARBON DIOXIDE UNDER VARIOUS CONDITIONS (TEST 1)[a]

Compound no.	Compound	Percent recovery							
		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8
1	Naphthalene	3.1	1.5	1.5	1.5	2.5	4.6	1.5	4.3
2	2-Methylnaphthalene	0.8	13.1	2.4	7.2	8.1	7.1	2.9	27.1
3	Acenaphthylene	13.1	20.9	10.5	31.4	30.4	34.6	6.3	54.5
4	Acenaphthene	19.9	35.9	16.5	45.7	45.9	55.4	7.5	77.5
5	Dibenzofuran	31.4	44.6	16.6	51.1	50.8	64.2	6.5	80.8
6	Fluorene	37.8	39.4	16.7	47.8	45.9	63.4	7.3	71.5
7	Phenanthrene	74.5	66.4	42.0	91.5	59.2	107.0	19.3	123.0
8	Anthracene	76.8	37.0	27.7	14.9	44.5	63.5	20.1	80.1
9	Fluoranthene	60.9	28.8	39.5	60.9	46.6	46.3	20.3	71.6
10	Pyrene	55.7	30.8	44.2	65.8	43.2	42.8	21.1	61.9
11	Benzo(a)anthracene	35.5	15.7	37.9	43.7	29.3	19.4	18.9	29.8
12	Chrysene	32.0	15.0	36.0	41.1	25.9	17.6	18.0	25.0
13	Benzo(b+k)fluoranthene	21.4	9.5	27.6	30.9	17.0	10.0	15.5	6.2
14	Benzo(a)pyrene	11.3	4.6	18.5	17.0	9.5	5.6	8.2	7.6
15	Pentachlorophenol	40.3	16.4	37.8	50.8	44.1	40.2	18.4	37.1

[a] The experimental conditions are given in Table 1.

TABLE 33. EXTRACTION OF SRS 103-100 WITH SUPERCRITICAL CARBON DIOXIDE UNDER VARIOUS CONDITIONS (TEST 2)[a]

Compound no.	Compound	Percent recovery							
		Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8
1	Naphthalene	67.9	30.9	18.5	3.1	77.2	49.4	52.5	12.3
2	2-Methylnaphthalene	90.2	24.2	67.6	1.6	101	74.1	75.7	33.8
3	Acenaphthylene	57.6	26.2	47.1	5.2	62.8	57.6	47.1	47.1
4	Acenaphthene	98.6	54.7	80.9	8.9	108	62.7	80.2	88.0
5	Dibenzofuran	105	53.7	87.9	7.5	110	67.4	85.3	104.0
6	Fluorene	87.0	48.4	78.0	10.8	95.1	64.0	70.3	93.1
7	Phenanthrene	124	78.5	129.0	49.2	153	130	92.1	174
8	Anthracene	85.1	59.5	90.8	42.2	101	96.4	60.7	123
9	Fluoranthene	81.3	51.4	97.7	74.4	109	113	50.3	137
10	Pyrene	57.5	37.9	74.7	58.7	74.2	85.0	35.6	96.8
11	Benzo(a)anthracene	36.5	24.2	59.1	38.1	46.4	54.8	19.4	59.9
12	Chrysene	37.7	23.6	63.6	36.7	46.1	49.8	21.9	56.9
13	Benzo(b+k)fluoranthene	30.3	9.2	52.0	17.8	29.6	7.9	7.2	13.2
14	Benzo(a)pyrene	16.5	2.1	31.9	7.2	17.5	2.0	8.2	15.4
15	Pentachlorophenol	89.4	46.5	55.9	69.2	147	117	42.7	144

[a] The experimental conditions are given in Table 2.

TABLE 34. GROUP DIFFERENCES FOR EACH OF THE TARGET ANALYTES UNDER VARIOUS EXPERIMENTAL CONDITIONS (TEST 1)[a]

Compound no.	Compound	V_P	V_D	V_M	V_V	V_S	V_T	V_C
1	Naphthalene	1.33	-0.73	0.82	-0.08	-1.63	-0.58	-0.22
2	2-Methylnaphthalene	7.90	5.10	7.60	-2.30	-4.00	-6.90	5.70
3	Acenaphthylene	12.48	0.93	20.28	3.03	-5.93	-14.27	7.73
4	Acenaphthene	17.08	-2.47	31.18	5.68	-8.58	-18.43	11.83
5	Dibenzofuran	14.65	-9.00	33.85	4.85	-10.00	-20.55	9.90
6	Fluorene	11.60	-10.80	28.60	4.45	-12.25	-19.05	4.30
7	Phenanthrene	8.53	-7.83	48.23	4.12	-27.53	-28.38	-0.42
8	Anthracene	12.95	-19.75	6.60	-15.85	-32.90	-17.00	3.50
9	Fluoranthene	-1.33	2.45	10.08	2.93	-15.42	-26.28	-0.47
10	Pyrene	-6.88	5.12	9.27	6.62	-10.93	-21.93	-1.32
11	Benzo(a)anthracene	-8.85	7.60	-3.25	7.60	-3.75	-11.60	-1.20
12	Chrysene	-9.40	7.40	-3.30	7.65	-2.65	-9.35	-1.70
13	Benzo(b+k)fluoranthene	-10.17	5.58	-6.23	8.23	1.92	-3.22	-4.37
14	Benzo(a)pyrene	-5.13	5.08	-3.18	4.73	-0.93	-2.13	-0.48
15	Pentachlorophenol	-1.37	0.77	-0.98	15.18	-6.43	-14.88	-3.57

[a] Group differences were calculated using Equations 1 through 7 (page 14 of this report).

TABLE 35. GROUP DIFFERENCES FOR EACH OF THE TARGET ANALYTES UNDER VARIOUS EXPERIMENTAL CONDITIONS (TEST 2)[a]

Compound no.	Compound	v_P	v_D	v_F	v_G	v_M	v_B	v_E
1	Naphthalene	17.75	-34.75	-30.10	-3.85	3.90	-2.30	-8.50
2	2-Methylnaphthalene	25.25	-27.70	-50.20	5.10	-15.80	3.75	-3.75
3	Acenaphthylene	19.63	-14.42	-19.63	-1.33	-17.03	1.33	3.92
4	Acenaphthene	23.95	-16.50	-38.35	-15.25	-19.60	-6.25	20.30
5	Dibenzofuran	28.15	-12.85	-38.90	-18.80	-26.95	-8.05	22.60
6	Fluorene	24.57	-10.58	-28.53	-12.73	-24.38	-6.32	20.62
7	Phenanthrene	42.10	-10.30	-16.60	-1.85	-46.05	-17.65	34.80
8	Anthracene	25.88	-6.32	-4.12	0.53	-32.98	-10.97	22.47
9	Fluoranthene	26.13	1.18	9.38	18.53	-35.98	-22.33	19.03
10	Pyrene	15.67	2.78	9.12	16.23	-26.93	-13.53	11.73
11	Benzo(a)anthracene	5.65	3.65	3.90	14.60	-20.55	-5.85	10.20
12	Chrysene	3.27	5.48	-0.58	14.03	-19.93	-4.63	11.03
13	Benzo(b+k)fluoranthene	-12.85	3.30	-17.75	11.85	-9.90	-3.65	10.20
14	Benzo(a)pyrene	-3.65	6.15	-11.85	4.10	-7.70	-3.10	8.25
15	Pentachlorophenol	47.43	-22.03	10.42	16.63	-25.23	-46.88	18.78

[a] Group differences were calculated using Equations 1 through 7 (page 14 of this report).

TABLE 36. VARIABLE RANKS BASED ON RELATIVE CHANGES

		Compound number															
	Variable	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**Sum**
1	Pressure	6	5	5	5	5	3	3	3	2	4	6	7	7	7	2	70
2	Temperature	5	2	1	1	3	4	4	6	3	2	5	4	3	6	1	50
3	Moisture	4	4	6	6	6	6	7	2	5	5	2	3	6	4	3	69
4	Cell volume	1	1	2	2	1	2	2	4	4	3	4	5	5	5	6	47
5	Sample size	7	6	3	3	4	5	5	7	6	6	3	2	1	2	5	65
6	Time	3	7	7	7	7	7	6	5	7	7	7	6	2	3	7	88
7	Modifier volume	2	3	4	4	2	1	1	1	1	1	1	1	4	1	4	31

TABLE 37. DATA SORTED BY VARIABLE AND COMPOUND (TEST 1)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Pressure	1.31	40
2	Pressure	7.85	70
3	Pressure	12.43	40
4	Pressure	17.06	37
5	Pressure	14.60	29
6	Pressure	11.63	25
7	Pressure	8.34	11
8	Pressure	12.97	25
9	Pressure	-1.35	-3
10	Pressure	-6.87	-16
11	Pressure	-8.82	-36
12	Pressure	-9.40	-43
13	Pressure	-10.20	-84
14	Pressure	-5.14	-67
15	Pressure	-0.83	-2
1	Temperature	-0.69	-31
2	Temperature	5.11	52
3	Temperature	0.92	4
4	Temperature	-2.48	-7
5	Temperature	-9.01	-23
6	Temperature	-10.83	-30
7	Temperature	-7.85	-11
8	Temperature	-19.73	-55
9	Temperature	2.44	5
10	Temperature	5.18	11
11	Temperature	7.59	23
12	Temperature	7.43	25
13	Temperature	5.59	28
14	Temperature	5.09	40
15	Temperature	0.26	1
1	Moisture	0.85	28
2	Moisture	7.61	68
3	Moisture	20.29	57
4	Moisture	31.20	58
5	Moisture	33.85	56
6	Moisture	28.62	52
7	Moisture	48.05	50
8	Moisture	6.58	13
9	Moisture	10.06	19
10	Moisture	9.29	18
11	Moisture	-3.24	-12
12	Moisture	-3.32	-13
13	Moisture	-6.22	-44
14	Moisture	-3.19	-37
15	Moisture	1.45	4

(continued)

TABLE 37. (Continued)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Cell volume	-0.08	-3
2	Cell volume	-2.29	-37
3	Cell volume	3.01	11
4	Cell volume	5.65	14
5	Cell volume	4.86	11
6	Cell volume	4.43	10
7	Cell volume	4.14	6
8	Cell volume	-15.82	-42
9	Cell volume	2.91	6
10	Cell volume	6.63	14
11	Cell volume	7.59	23
12	Cell volume	7.63	25
13	Cell volume	8.22	38
14	Cell volume	4.68	37
15	Cell volume	14.66	34
1	Sample size	-1.62	-91
2	Sample size	-3.99	-74
3	Sample size	-5.89	-26
4	Sample size	-8.58	-25
5	Sample size	-9.99	-26
6	Sample size	-12.26	-35
7	Sample size	-27.35	-46
8	Sample size	-32.88	-113
9	Sample size	-15.41	-39
10	Sample size	-10.94	-27
11	Sample size	-3.80	-14
12	Sample size	-2.65	-11
13	Sample size	1.94	11
14	Sample size	-0.93	-9
15	Sample size	-5.91	-18
1	Time	-0.54	-23
2	Time	-6.88	-176
3	Time	-14.27	-79
4	Time	-18.47	-64
5	Time	-20.58	-62
6	Time	-19.07	-60
7	Time	-28.34	-48
8	Time	-17.00	-46
9	Time	-26.31	-78
10	Time	-21.93	-63
11	Time	-11.60	-50
12	Time	-9.32	-43
13	Time	-3.19	-20
14	Time	-2.11	-23
15	Time	-15.39	-56

(continued)

TABLE 37. (Concluded)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Modifier volume	-0.23	-9
2	Modifier volume	5.68	56
3	Modifier volume	7.72	27
4	Modifier volume	11.82	27
5	Modifier volume	9.91	21
6	Modifier volume	4.33	10
7	Modifier volume	-0.40	-1
8	Modifier volume	3.50	7
9	Modifier volume	-0.53	-1
10	Modifier volume	-1.31	-3
11	Modifier volume	-1.20	-4
12	Modifier volume	-1.71	-7
13	Modifier volume	-4.38	-29
14	Modifier volume	-0.46	-5
15	Modifier volume	-4.09	-12

TABLE 38. DATA SORTED BY ABSOLUTE PERCENT CHANGE BY COMPOUND (TEST 1)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Cell volume	-0.08	-3
1	Modifier volume	-0.23	-9
1	Time	-0.54	-23
1	Moisture	0.85	28
1	Temperature	-0.69	-31
1	Pressure	1.31	40
1	Sample size	-1.62	-91
2	Cell volume	-2.29	-37
2	Temperature	5.11	52
2	Modifier volume	5.68	56
2	Moisture	7.61	68
2	Pressure	7.85	70
2	Sample size	-3.99	-74
2	Time	-6.88	-176
3	Temperature	0.92	4
3	Cell volume	3.01	11
3	Sample size	-5.89	-26
3	Modifier volume	7.72	27
3	Pressure	12.43	40
3	Moisture	20.29	57
3	Time	-14.27	-79
4	Temperature	-2.48	-7
4	Cell volume	5.65	14
4	Sample size	-8.58	-25
4	Modifier volume	11.82	27
4	Pressure	17.06	37
4	Moisture	31.20	58
4	Time	-18.47	-64
5	Cell volume	4.86	11
5	Modifier volume	9.91	21
5	Temperature	-9.01	-23
5	Sample size	-9.99	-26
5	Pressure	14.60	29
5	Moisture	33.85	56
5	Time	-20.58	-62

(continued)

TABLE 38. (Continued)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
6	Modifier volume	4.33	10
6	Cell volume	4.43	10
6	Pressure	11.63	25
6	Temperature	-10.83	-30
6	Sample size	-12.26	-35
6	Moisture	23.62	52
6	Time	-19.07	-60
7	Modifier volume	-0.40	-1
7	Cell volume	4.14	6
7	Pressure	8.34	11
7	Temperature	-7.85	-11
7	Sample size	-27.35	-46
7	Time	-28.34	-48
7	Moisture	48.05	50
8	Modifier volume	3.50	7
8	Moisture	6.58	13
8	Pressure	12.97	25
8	Cell volume	-15.82	-42
8	Time	-17.00	-46
8	Temperature	-19.73	-55
8	Sample size	-32.88	-113
9	Modifier volume	-0.53	-1
9	Pressure	-1.35	-3
9	Temperature	2.44	5
9	Cell volume	2.91	6
9	Moisture	10.06	19
9	Sample size	-15.41	-39
9	Time	-26.31	-78
10	Modifier volume	-1.31	-3
10	Temperature	5.18	11
10	Cell volume	6.63	14
10	Pressure	-6.87	-16
10	Moisture	9.29	18
10	Sample size	-10.94	-27
10	Time	-21.93	-63

(continued)

TABLE 38. (Concluded)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
11	Modifier volume	-1.20	-4
11	Moisture	-3.24	-12
11	Sample size	-3.80	-14
11	Temperature	7.59	23
11	Cell volume	7.59	23
11	Pressure	-8.82	-36
11	Time	-11.60	-50
12	Modifier volume	-1.71	-7
12	Sample size	-2.65	-11
12	Moisture	-3.32	-13
12	Temperature	7.43	25
12	Cell volume	7.63	25
12	Time	-9.32	-43
12	Pressure	-9.40	-43
13	Sample size	1.94	11
13	Time	-3.19	-20
13	Temperature	5.59	28
13	Modifier volume	-4.38	-29
13	Cell volume	8.22	38
13	Moisture	-6.22	-44
13	Pressure	-10.20	-84
14	Modifier volume	-0.46	-5
14	Sample size	-0.93	-9
14	Time	-2.11	-23
14	Moisture	-3.19	-37
14	Cell volume	4.68	37
14	Temperature	5.09	40
14	Pressure	-5.14	-67
15	Temperature	0.26	1
15	Pressure	-0.83	-2
15	Moisture	1.45	4
15	Modifier volume	-4.09	-12
15	Sample size	-5.91	-18
15	Cell volume	14.66	34
15	Time	-15.39	-56

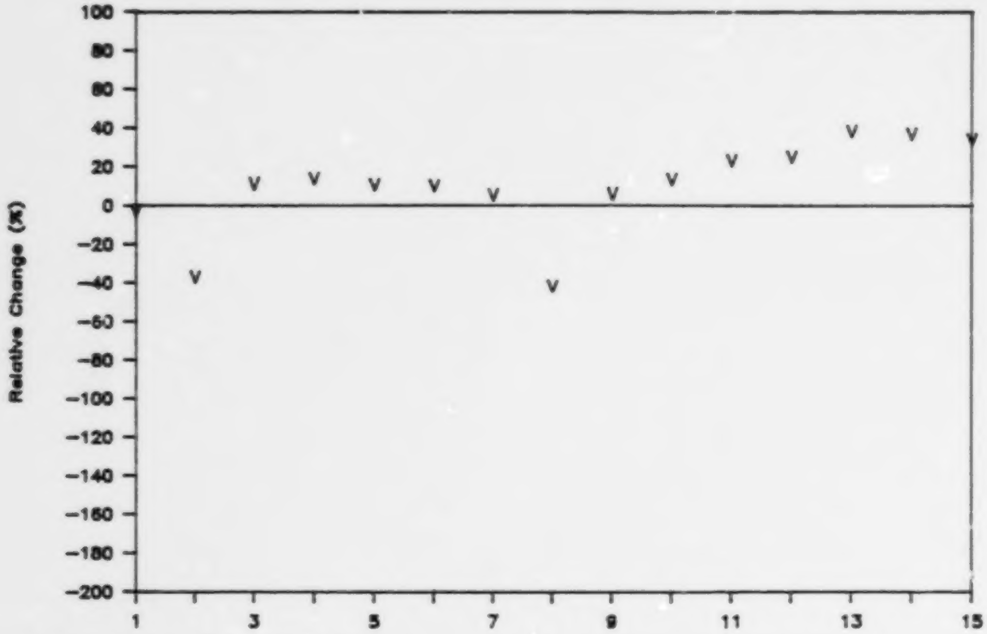


Figure 35. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is cell volume (V).

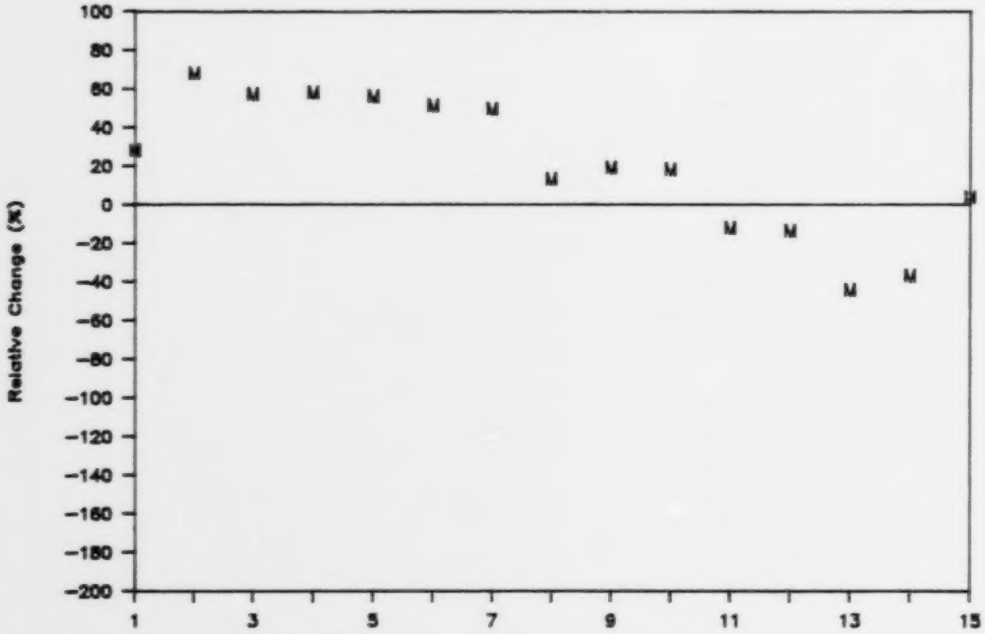


Figure 36. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is moisture (M).

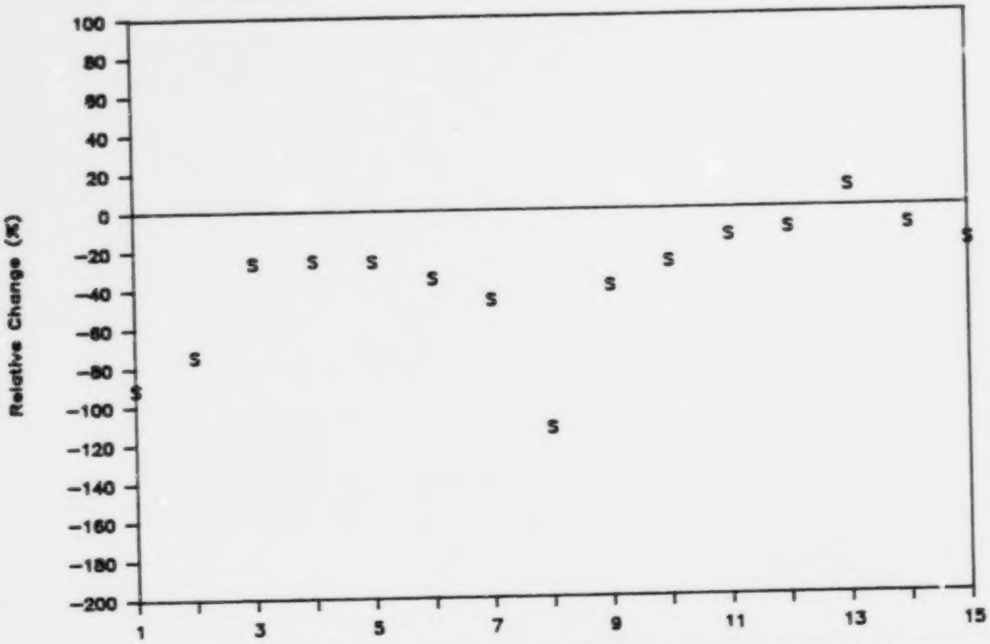


Figure 37. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is sample size (S).

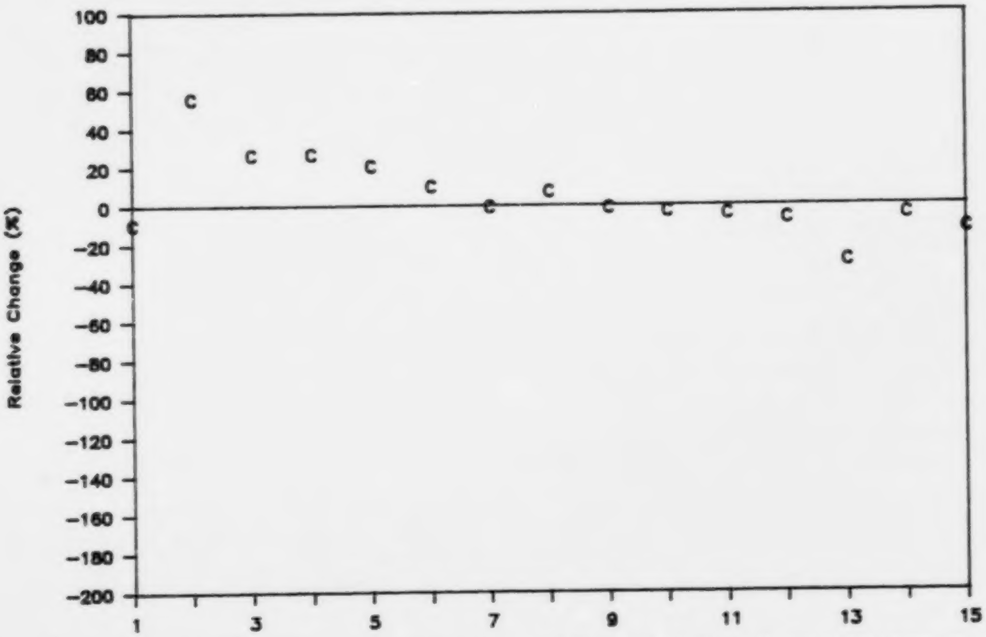


Figure 38. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is modifier volume (C).

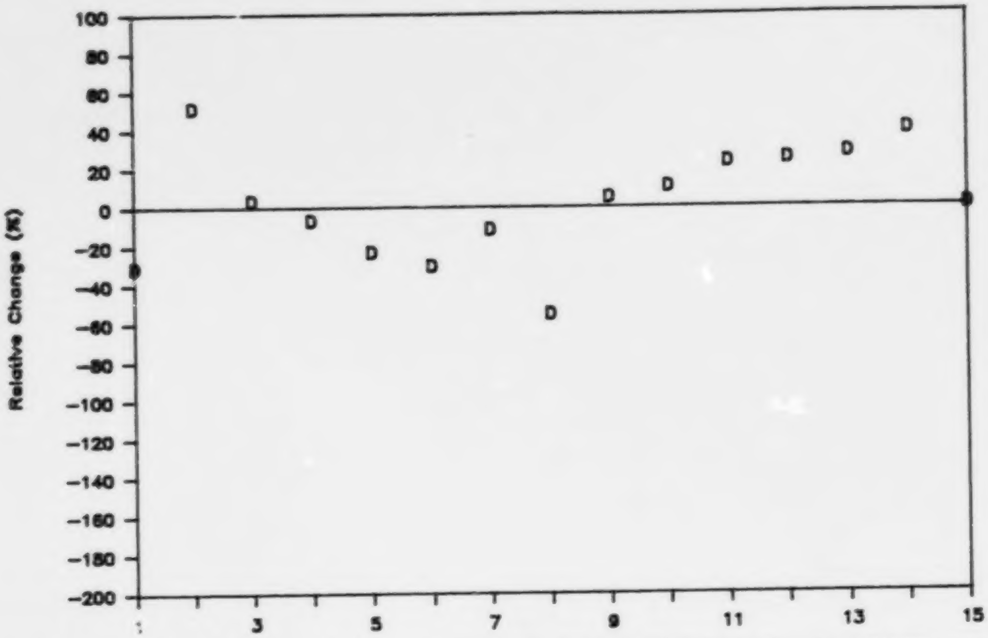


Figure 39. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is temperature (D).

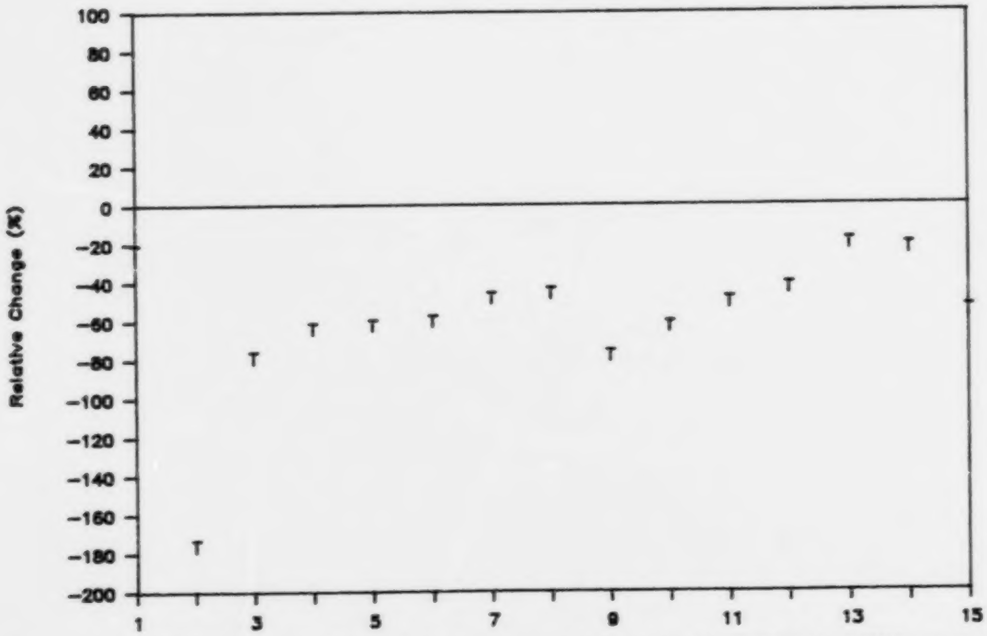


Figure 40. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is time (T).

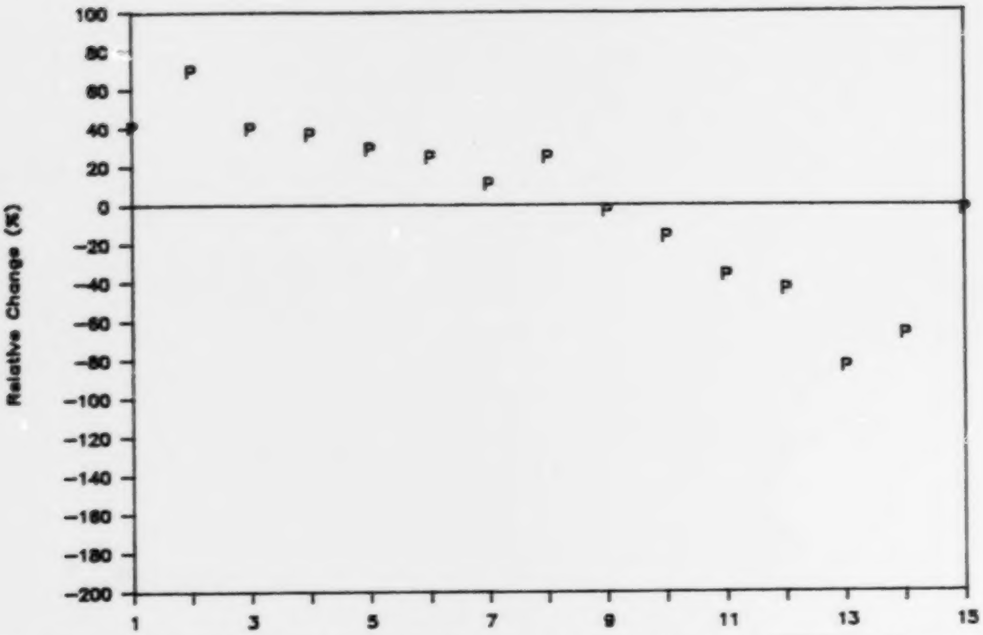


Figure 41. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variable is pressure (P).

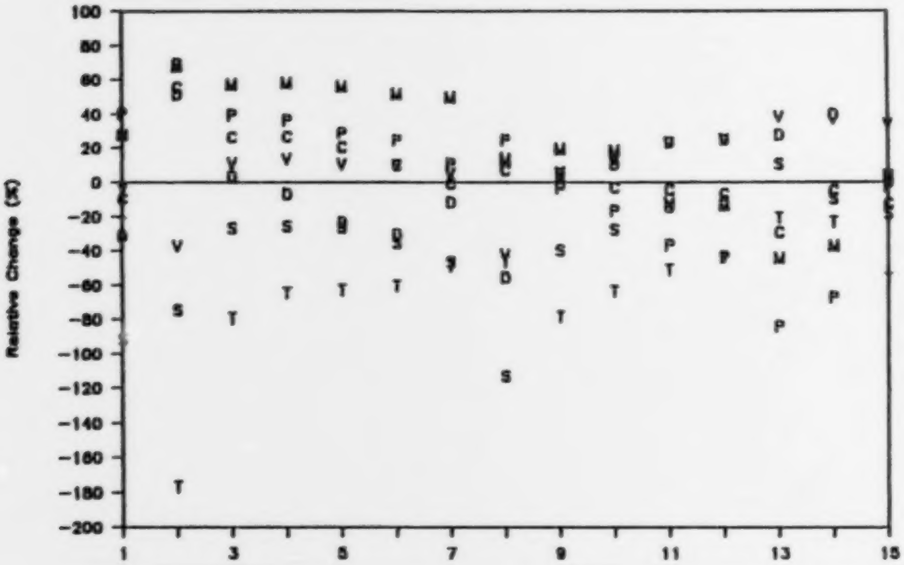


Figure 42. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 1). The variables are identified as follows: pressure (P), temperature (D), moisture (M), cell volume (V), sample size (S), time (T), modifier volume (C). The 15 compounds are those listed in Table 32.

TABLE 39. VARIABLE RANKS BASED ON RELATIVE CHANGES (TEST 2)

Variable	Compound number															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	Sum
Pressure	5	5	4	5	5	5	6	6	5	4	3	2	6	3	6	70
Temperature	7	6	5	4	2	2	2	3	1	1	1	4	1	4	4	47
Volume of toluene	6	7	7	7	7	7	3	2	2	2	2	1	7	7	1	68
Volume of collection solvent	3	3	2	2	4	3	1	1	3	5	6	6	4	1	2	46
Moisture	2	4	6	6	6	6	7	7	7	7	7	7	5	6	5	88
Cell volume	1	1	2	2	1	2	2	4	4	3	4	5	5	5	6	47
Glass beads	1	1	1	1	1	1	4	4	6	6	4	3	2	2	7	44
Static extraction time	4	2	3	3	3	4	5	5	4	3	5	5	3	5	3	57

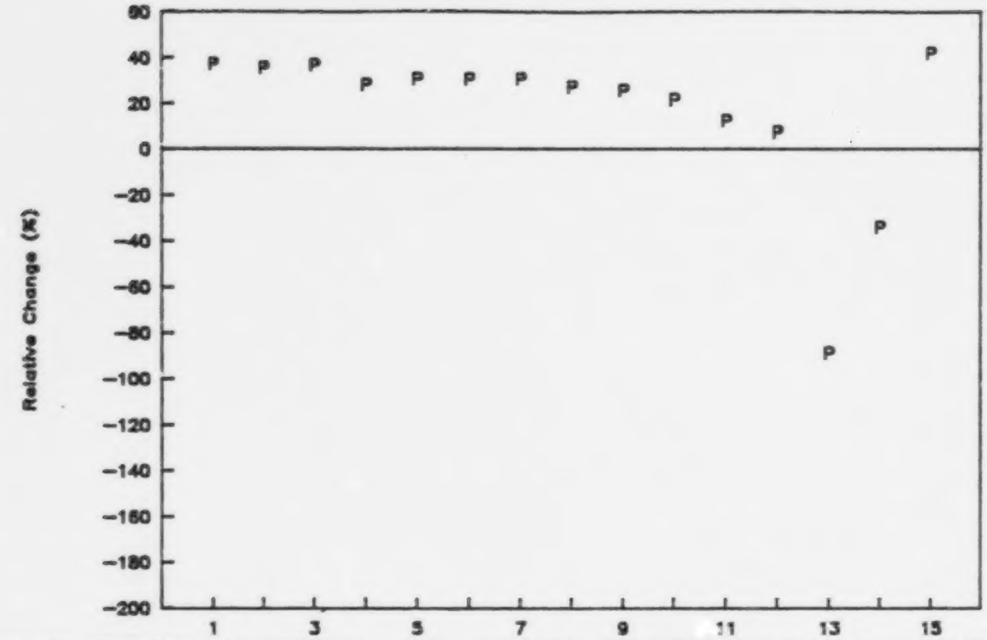


Figure 43. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is pressure (P).

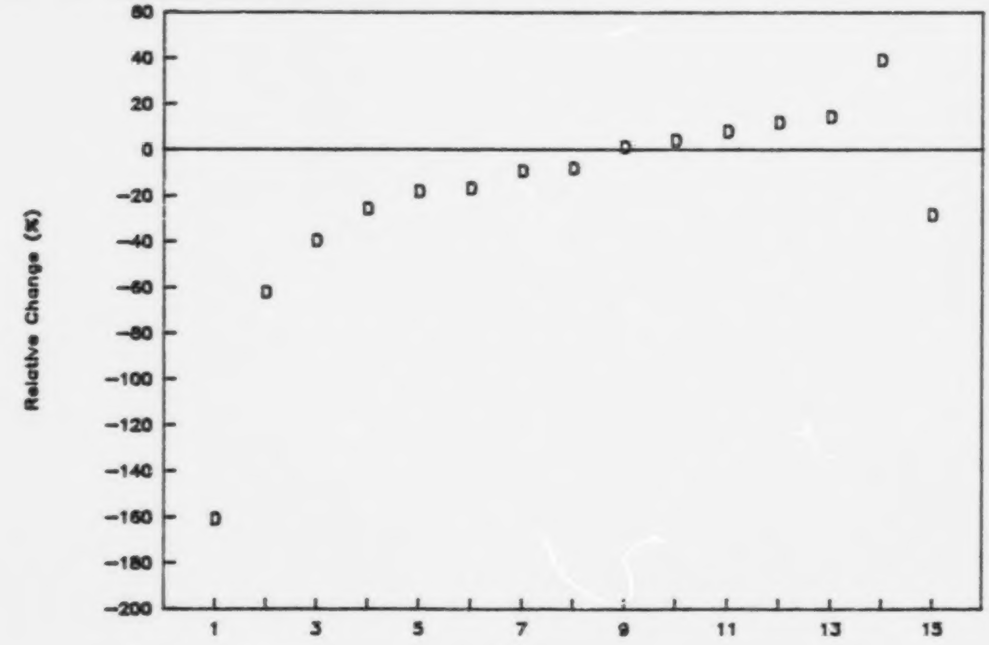


Figure 44. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is temperature (D).

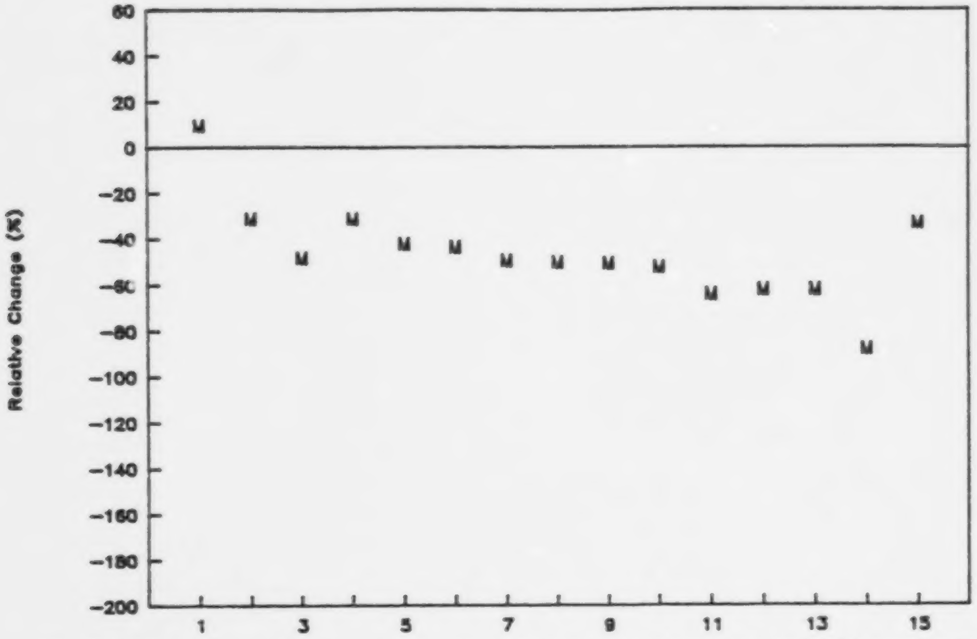


Figure 45. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is moisture (M).

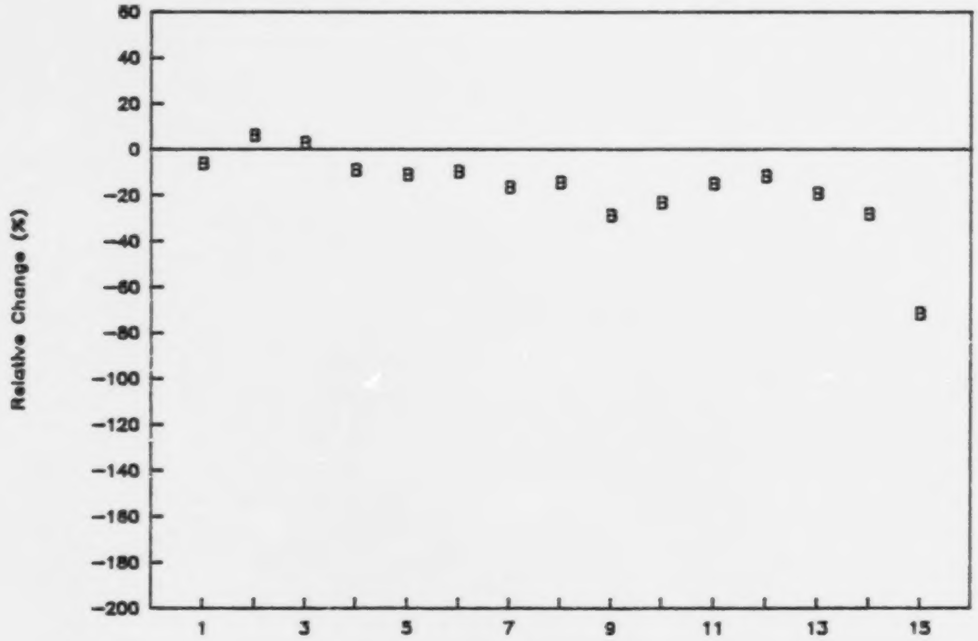


Figure 46. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is glass beads (B).

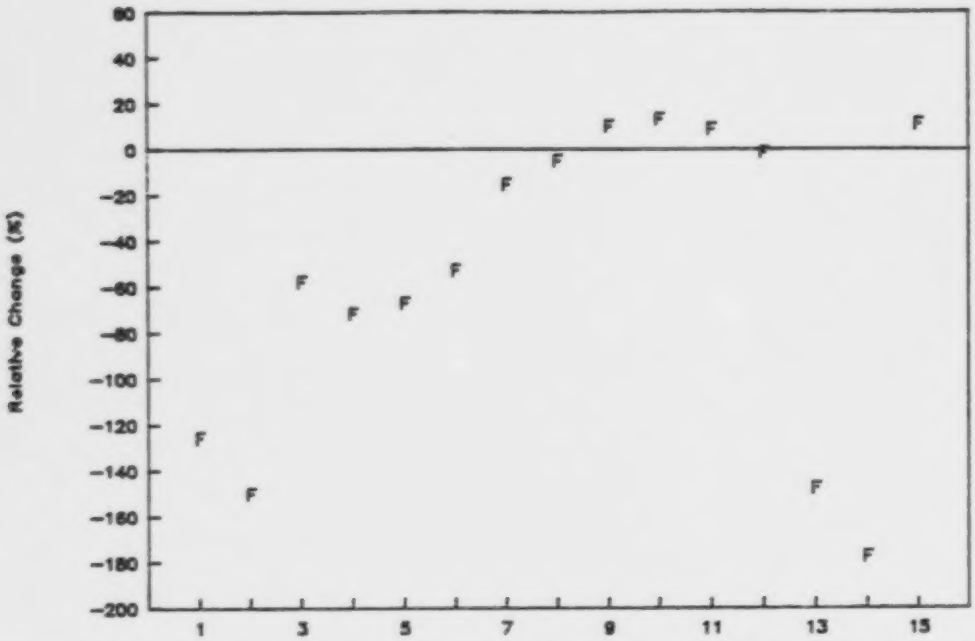


Figure 47. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is volume of toluene (F).

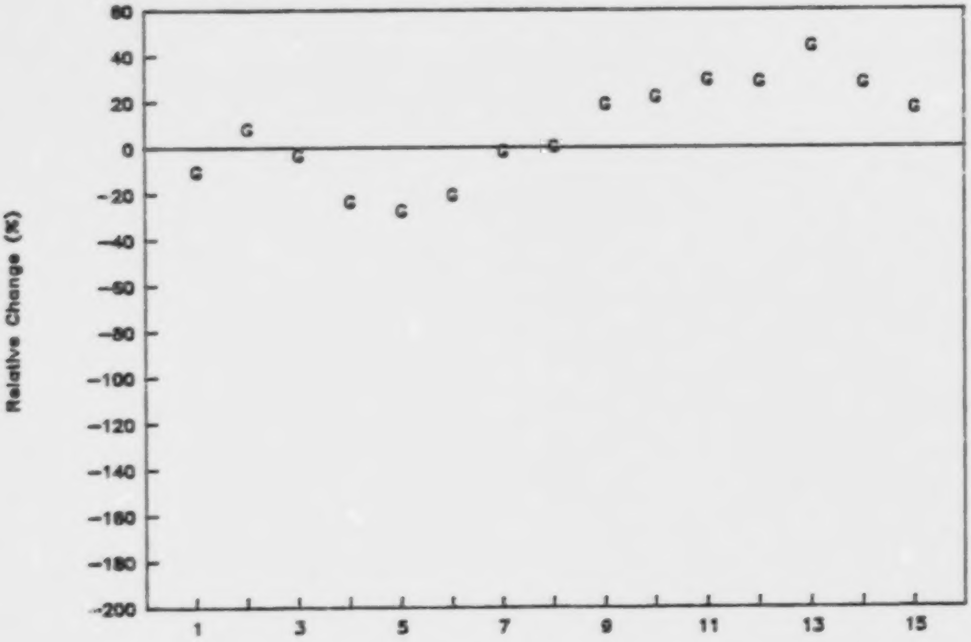


Figure 48. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is volume of collection solvent (G).

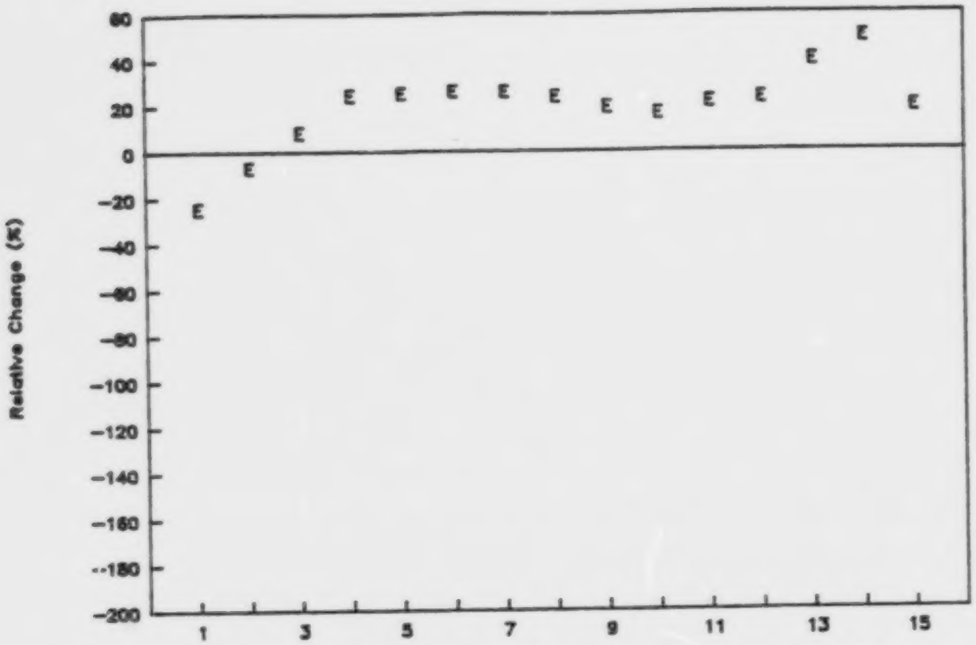


Figure 49. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variable is static extraction time (E).

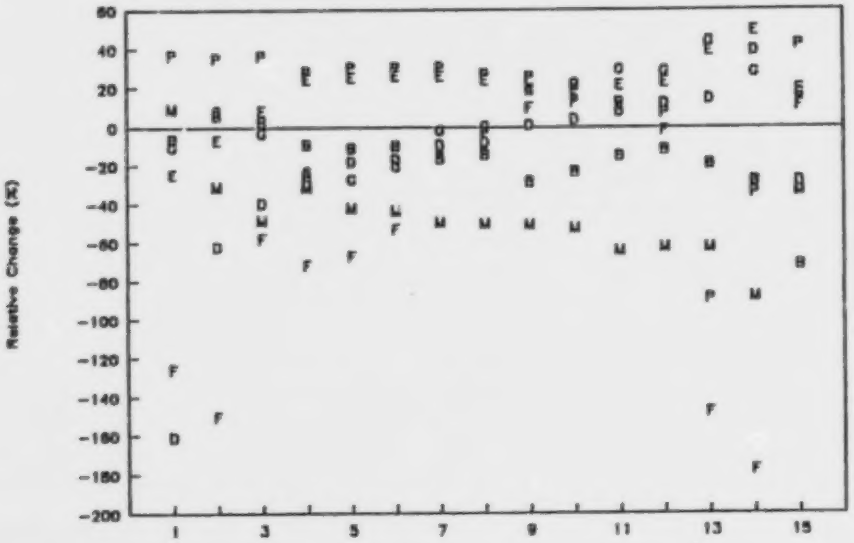


Figure 50. Relative changes in percent recovery (when going from low to high) across the 15 target analytes (Test 2). The variables are identified as follows: pressure (P), temperature (D), volume of toluene as modifier (F), volume of collection solvent (G), moisture (M), glass beads (B), and static extraction time (E). The 15 compounds are those listed in Table 33.

TABLE 40. DATA SORTED BY VARIABLE AND COMPOUND (TEST 2)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Pressure	17.75	37
2	Pressure	25.25	35
3	Pressure	19.63	37
4	Pressure	23.95	28
5	Pressure	28.15	31
6	Pressure	24.58	30
7	Pressure	42.10	31
8	Pressure	25.88	27
9	Pressure	26.13	26
10	Pressure	15.70	22
11	Pressure	5.65	13
12	Pressure	3.27	7
13	Pressure	-12.85	-89
14	Pressure	-3.65	-34
15	Pressure	47.43	42
1	Temperature	-34.75	-161
2	Temperature	-27.70	-62
3	Temperature	-14.42	-39
4	Temperature	-16.50	-26
5	Temperature	-12.85	-18
6	Temperature	-10.58	-17
7	Temperature	-10.30	-9
8	Temperature	-6.33	-8
9	Temperature	1.17	1
10	Temperature	2.80	4
11	Temperature	3.65	8
12	Temperature	5.48	12
13	Temperature	3.30	15
14	Temperature	6.15	39
15	Temperature	-22.02	-28
1	Volume of toluene	-30.10	-126
2	Volume of toluene	-50.20	-150
3	Volume of toluene	-19.63	-58
4	Volume of toluene	-38.35	-72
5	Volume of toluene	-38.90	-67
6	Volume of toluene	-28.52	-53
7	Volume of toluene	-16.60	-15
8	Volume of toluene	-4.13	-5
9	Volume of toluene	9.38	10
10	Volume of toluene	9.10	13
11	Volume of toluene	3.90	9
12	Volume of toluene	-0.58	-1
13	Volume of toluene	-17.75	-148
14	Volume of toluene	-11.85	-178
15	Volume of toluene	10.42	11

(continued)

TABLE 40. (Continued)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Collection volume	-3.85	-10
2	Collection volume	5.10	8
3	Collection volume	-1.33	-3
4	Collection volume	-15.25	-23
5	Collection volume	-18.80	-28
6	Collection volume	-12.73	-21
7	Collection volume	-1.85	-2
8	Collection volume	0.52	1
9	Collection volume	18.53	19
10	Collection volume	16.20	22
11	Collection volume	14.60	29
12	Collection volume	14.02	29
13	Collection volume	11.85	44
14	Collection volume	4.10	28
15	Collection volume	16.63	17
1	Moisture	3.90	10
2	Moisture	-15.80	-31
3	Moisture	-17.03	-48
4	Moisture	-19.60	-31
5	Moisture	-26.95	-42
6	Moisture	-24.38	-43
7	Moisture	-46.05	-49
8	Moisture	-32.98	-50
9	Moisture	-35.97	-50
10	Moisture	-26.90	-52
11	Moisture	-20.55	-64
12	Moisture	-19.92	-62
13	Moisture	-9.90	-62
14	Moisture	-7.70	-88
15	Moisture	-25.23	-33
1	Glass Beads	-2.30	-6
2	Glass Beads	3.75	6
3	Glass Beads	1.33	3
4	Glass Beads	-6.25	-9
5	Glass Beads	-8.05	-11
6	Glass Beads	-6.33	-10
7	Glass Beads	-17.65	-16
8	Glass Beads	-10.98	-14
9	Glass Beads	-22.33	-29
10	Glass Beads	-13.50	-23
11	Glass Beads	-5.85	-15
12	Glass Beads	-4.63	-12
13	Glass Beads	-3.65	-19
14	Glass Beads	-3.10	-28
15	Glass Beads	-46.88	-72

(continued)

TABLE 40. (Concluded)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Static extraction time	-8.50	-24
2	Static extraction time	-3.75	-7
3	Static extraction time	3.92	9
4	Static extraction time	20.30	24
5	Static extraction time	22.60	25
6	Static extraction time	20.63	26
7	Static extraction time	34.80	26
8	Static extraction time	22.48	24
9	Static extraction time	19.03	19
10	Static extraction time	11.70	17
11	Static extraction time	10.20	22
12	Static extraction time	11.02	23
13	Static extraction time	10.20	39
14	Static extraction time	8.25	49
15	Static extraction time	18.77	19

TABLE 41. DATA SORTED BY ABSOLUTE PERCENT CHANGE BY COMPOUND (TEST 2)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
1	Glass beads	-2.30	-6
1	Moisture	3.90	10
1	Collection volume	-3.85	-10
1	Static extraction time	-8.50	-24
1	Pressure	17.75	37
1	Volume of toluene	-30.10	-126
1	Temperature	-34.75	-161
2	Glass beads	3.75	6
2	Static extraction time	-3.75	-7
2	Collection volume	5.10	8
2	Moisture	-15.80	-31
2	Pressure	25.25	35
2	Temperature	-27.70	-62
2	Volume of toluene	-50.20	-150
3	Glass beads	1.33	3
3	Collection volume	-1.33	-3
3	Static extraction time	3.92	9
3	Pressure	19.63	37
3	Temperature	-14.42	-39
3	Moisture	-17.03	-48
3	Volume of toluene	-19.63	-58
4	Glass beads	-6.25	-9
4	Collection volume	-15.25	-23
4	Static extraction time	20.30	24
4	Temperature	-16.50	-26
4	Pressure	23.95	28
4	Moisture	-19.60	-31
4	Volume of toluene	-38.35	-72
5	Glass beads	-8.05	-11
5	Temperature	-12.85	-18
5	Static extraction time	22.60	25
5	Collection volume	-18.80	-28
5	Pressure	28.15	31
5	Moisture	-26.95	-42
5	Volume of toluene	-38.90	-67

(continued)

TABLE 41. (Continued)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
6	Glass beads	-6.33	-10
6	Temperature	-10.58	-17
6	Collection volume	-12.73	-21
6	Static extraction time	20.63	26
6	Pressure	24.58	30
6	Moisture	-24.38	-43
6	Volume of toluene	-28.52	-53
7	Collection volume	-1.85	-2
7	Temperature	-10.30	-9
7	Volume of toluene	-16.60	-15
7	Glass beads	-17.65	-16
7	Static extraction time	34.80	26
7	Pressure	42.10	31
7	Moisture	-46.05	-49
8	Collection volume	0.52	1
8	Volume of toluene	-4.13	-5
8	Temperature	-6.33	-8
8	Glass beads	-10.98	-14
8	Static extraction time	22.48	24
8	Pressure	25.88	27
8	Moisture	-32.98	-50
9	Temperature	1.17	1
9	Volume of toluene	9.38	10
9	Collection volume	18.53	19
9	Static extraction time	19.03	19
9	Pressure	26.13	26
9	Glass beads	-22.33	-29
9	Moisture	-35.97	-50
10	Temperature	2.80	4
10	Volume of toluene	9.10	13
10	Static extraction time	11.70	17
10	Pressure	15.70	22
10	Collection volume	16.20	22
10	Glass beads	-13.50	-23
10	Moisture	-26.90	-52

(continued)

TABLE 41. (Concluded)

Compound no.	Variable	Effect (low-high)	Relative change (percent)
11	Temperature	3.65	8
11	Volume of toluene	3.90	9
11	Pressure	5.65	13
11	Glass beads	-5.85	-15
11	Static extraction time	10.20	22
11	Collection volume	14.60	29
11	Moisture	-20.55	-64
12	Volume of toluene	-0.58	-1
12	Pressure	3.27	7
12	Glass beads	-4.63	-12
12	Temperature	5.48	12
12	Static extraction time	11.02	23
12	Collection volume	14.02	29
12	Moisture	-19.92	-62
13	Temperature	3.30	15
13	Glass beads	-3.65	-19
13	Static extraction time	10.20	39
13	Collection volume	11.85	44
13	Moisture	-9.90	-62
13	Pressure	-12.85	-89
13	Volume of toluene	-17.75	-148
14	Collection volume	4.10	28
14	Glass beads	-3.10	-28
14	Pressure	-3.65	-34
14	Temperature	6.15	39
14	Static extraction time	8.25	49
14	Moisture	-7.70	-88
14	Volume of toluene	-11.85	-178
15	Volume of toluene	10.42	11
15	Collection volume	16.63	17
15	Static extraction time	18.77	19
15	Temperature	-22.02	-28
15	Moisture	-25.23	-33
15	Pressure	47.43	42
15	Glass beads	-46.88	-72

From the experiments in Test 1, we concluded that the four variables time, pressure, moisture, and sample size should be further investigated. Pressure and moisture were also identified as being important variables in the experiments conducted in Test 2. Therefore, we designed a full factorial experiment in which the four variables were investigated at two levels. There were a total of 16 experiments, each performed in duplicate. The sample used to perform these experiments was again SRS 103-100. The recovery data for the 16 experiments (the duplicates are identified with letters A and B) are presented in Table 42. From the recovery data in Table 42, we established the effect of the individual variables, the interaction between two variables, and the interaction between three variables. Table 43 gives the significance levels from the analysis of variance (ANOVA) for each of the 15 compounds known to be present in the SRS 103-100. The four-way interaction (time x pressure x moisture x sample size) was not considered in ANOVA.

5.3 MULTIVESSEL SETUP FOR PARALLEL SFE

5.3.1 Evaluation of Two-Vessel-Extraction Setup

Thirty-six nitroaromatic compounds (Table 44) were spiked on sand and extracted in duplicate with carbon dioxide under supercritical conditions using the two-extraction-vessel setup. Figures 51 and 52 show the recoveries of the 36 compounds for the 4 experiments. The agreement between the duplicate extractions performed in parallel was excellent (within 10 percent). By examining the data in Figures 51 and 52, we concluded that the more volatile nitroaromatics (Compounds 1 through 17) were recovered quantitatively at lower, but not at higher, pressures, and that it was not advantageous to use higher pressures.

Nineteen haloethers (Table 45) were spiked on sand and extracted with carbon dioxide under supercritical conditions. Figure 53 shows the recoveries of the 19 compounds for the 6 experiments. The agreement between the duplicate extractions performed in parallel was not as good as in the case of the nitroaromatics, however it was within 15 percent for most compounds.The lowest recoveries were observed when the samples were extracted at 250 atm and the sand was spiked in an aluminum cup rather than in the extraction vessel.

5.3.2 Evaluation of Four-Vessel-Extraction Setup

Spiked Sand

Tables 46 through 49 summarize the data for 19 haloethers, 42 organochlorine pesticides, 46 organophosphorus pesticides, and 30 other target analytes spiked onto sand at the levels indicated in the corresponding tables and extracted with supercritical carbon dioxide. The experimental conditions (pressure, temperature, extraction time) were established previously using our one-extraction-vessel and two-extraction-vessel setups (16,17). This time, we were mostly interested in establishing the reproducibility of the extraction technique using the four-extraction vessel setup.

The results presented in Table 46 for the 19 haloethers indicate that ten compounds exhibited recoveries greater than 85 percent, five compounds were in the range of 75 to 84 percent, and four compounds were in the range of 46 to 74 percent. Reproducibility of the extraction technique as measured by the percent relative standard deviation (RSD) of the four extractions ranged from 1.2 to 35.6 percent, with 12 compounds having RSDs under 10 percent, two compounds from 11 to 20 percent, and two compounds higher than 20 percent. The reproducibility of the extraction technique is certainly better than the RSD values given above

TABLE 42. METHOD OPTIMIZATION--PERCENT RECOVERIES

Compound	FD1A	FD1B	FD2A	FD2B	FD3A	FD3B	FD4A	FD4B	FD5A	FD5B
Naphthalene	54.0	57.9	42.4	34.7	30.9	34.7	73.3	81.0	52.5	58.6
2-Methylnaphthalene	94.6	102.7	66.4	74.5	78.5	78.5	104.7	102.7	90.2	85.3
Acenaphthylene	47.8	78.5	35.3	43.8	39.9	51.0	51.7	51.0	68.1	68.1
Acenaphthene	50.6	55.2	43.7	47.1	41.3	50.4	54.6	59.7	47.3	47.9
Dibenzofuran	104.2	113.6	90.0	96.9	85.1	103.8	112.4	123.0	97.4	98.7
Fluorene	85.4	95.8	72.7	86.1	74.2	91.2	95.3	100.9	83.7	84.3
Phenanthrene	108.9	122.1	111.2	132.9	97.3	140.6	153.7	124.4	137.2	142.8
Anthracene	116.4	132.1	94.5	111.7	95.7	117.3	129.7	132.7	114.2	104.7
Fluoranthene	103.5	121.1	83.4	99.6	93.7	108.4	113.3	121.1	104.7	109.4
Pyrene	96.1	110.1	79.7	96.7	85.2	103.2	107.0	113.3	100.7	103.6
Benzo(a)anthracene	70.9	78.4	65.0	79.9	65.5	82.8	78.4	83.3	63.5	66.7
Chrysene	80.4	85.9	76.6	85.9	76.6	91.8	87.1	93.9	62.6	64.3
Benzo(b+k)fluoranthene	55.1	66.6	63.3	77.3	70.7	81.4	60.0	69.1	3.3	3.3
Benzo(a)pyrene	23.1	24.4	33.4	29.6	36.0	43.7	16.7	24.4	5.1	5.1
Pentachlorophenol	154.1	169.7	107.0	134.7	125.9	150.3	146.4	165.8	102.8	115.0

TABLE 42. (Continued)

Compound	FD6A	FD6B	FD7A	FD7B	FD8A	FD8B	FD9A	FD9B	FD10A	FD10B
Naphthalene	57.9	57.9	46.3	61.7	49.4	58.6	46.3	61.7	52.5	58.6
2-Methylnaphthalene	88.6	90.6	82.5	82.5	85.3	85.3	82.5	84.5	88.6	85.3
Acenaphthylene	45.8	50.4	44.5	39.3	26.2	57.6	58.9	58.9	26.2	62.8
Acenaphthene	52.4	51.8	46.5	48.3	50.0	46.25	45.3	47.3	49.4	48.4
Dibenzofuran	107.9	106.7	95.7	99.3	102.9	95.1	93.2	97.3	101.6	99.7
Fluorene	91.2	92.0	84.6	87.4	82.3	79.5	83.6	87.9	82.5	84.3
Phenanthrene	144.5	153.0	132.1	139.8	113.7	109.4	129.0	117.4	121.1	118.0
Anthracene	116.4	124.1	105.2	111.4	118.0	110.9	106.0	118.2	111.8	113.5
Fluoranthene	110.4	123.0	103.5	110.4	109.4	110.9	111.3	117.2	120.3	122.7
Pyrene	106.8	112.3	96.0	102.5	98.7	95.2	97.8	102.0	107.5	107.5
Benzo(a)anthracene	77.9	79.9	70.4	72.9	62.3	60.7	69.9	70.4	81.3	79.4
Chrysene	85.4	85.0	74.9	79.1	60.9	56.2	76.2	76.2	89.6	83.2
Benzo(b+k)fluoranthene	78.1	69.9	55.9	47.7	3.3	3.3	4.1	47.7	65.8	57.9
Benzo(a)pyrene	36.0	6.4	18.0	6.4	5.1	5.1	6.4	6.4	41.2	31.9
Pentachlorophenol	160.6	164.5	119.0	139.9	105.7	110.9	123.2	132.1	177.2	174.1

TABLE 42. (Concluded)

Compound	FD11A	FD11B	FD12A	FD12B	FD13A	FD13B	FD14A	FD14B	FD15A	FD15B	FD16A	FD16B
Naphthalene	58.6	71.0	84.9	69.4	71.0	71.0	71.0	80.2	71.0	83.3	55.6	77.2
2-Methylnaphthalene	93.4	111.1	98.6	90.6	96.6	95.0	90.2	95.0	88.6	95.0	90.2	90.2
Acenaphthylene	62.8	78.5	32.7	32.7	73.3	68.1	68.1	73.3	26.2	78.5	26.2	26.2
Acenaphthene	51.3	62.5	51.4	51.8	59.3	55.2	52.1	57.4	53.6	59.2	53.6	59.5
Dibenzofuran	105.5	128.7	105.9	106.7	122.1	113.7	107.2	118.2	110.4	121.8	110.4	122.5
Fluorene	88.8	107.3	88.4	92.5	102.6	102.4	93.9	104.3	99.8	110.6	103.5	102.0
Phenanthrene	117.4	132.9	123.6	120.5	142.2	118.7	137.8	160.1	144.0	174.9	153.3	160.7
Anthracene	121.1	122.0	120.3	125.3	115.2	103.3	111.8	116.4	116.1	155.5	126.8	135.3
Fluoranthene	124.2	147.7	126.0	122.1	126.6	113.3	135.9	139.1	127.3	165.6	150.5	156.3
Pyrene	103.6	122.9	106.4	103.0	124.9	110.4	93.6	103.6	102.6	123.9	105.5	118.1
Benzo(a)anthracene	72.2	61.1	80.4	79.9	81.3	77.0	88.9	89.3	88.1	112.3	99.2	104.8
Chrysene	69.0	58.6	84.6	82.1	96.3	84.2	75.1	71.4	87.2	100.7	98.0	98.3
Benzo(b+k)fluoranthene	36.8	3.3	71.5	64.1	83.6	69.7	54.6	39.5	45.4	56.6	71.7	67.8
Benzo(a)pyrene	5.1	5.1	6.4	38.6	54.5	42.2	37.0	24.7	5.1	17.5	44.2	29.8
Pentachlorophenol	146.1	150.3	163.2	151.6	118.1	104.7	162.7	148.2	183.4	251.8	238.3	242.5

TABLE 43. SIGNIFICANCE LEVELS FROM ANOVA[a]

Variable/interaction[b]	Compound no.														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Time						0.0449				0.0262					
Pressure			0.0208						0.0411		0.0005	0.0001	0.0001	0.0041	0.0001
Moisture	0.0004							0.0367	0.0023		0.0051			0.0455	0.0033
Sample size	0.0065	0.0200		0.0120	0.0120	0.0106			0.0001	0.0389			0.0008		0.0330
Time x pressure	0.0159	0.0002		0.0449	0.0432										
Time x moisture															0.0343
Time x sample size		0.0003		0.0044	0.0044	0.0042							0.0116	0.0119	
Pressure x moisture															0.0065
Pressure x sample size											0.0021		0.0024	0.0269	0.0006
Moisture x sample size	0.0442	0.0043									0.0090	0.0001			0.0010
Time x pressure x moisture			0.0076				0.0402								
Time x pressure x sample size	0.0001	0.0001		0.0019	0.0019	0.0092		0.0053	0.0017	0.0465	0.0141				0.0001
Time x moisture x sample size		0.0422					0.0157								
Pressure x moisture x sample size							0.0153	0.0480	0.0312					0.0492	0.0017

[a] Four-way interaction time x pressure x moisture x sample size was not considered in ANOVA.
[b] The variable or interaction was not significant at 5 percent when cell is empty.

TABLE 44. PERCENT RECOVERIES OF NITROAROMATICS FROM SPIKED SAND[a]

Compound no.	Compound	Fraction 1		Fraction 2		Fraction 1	
		Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 3	Exp. 4
1	Nitrobenzene	44.5	42.4	0	0	0	0
2	o-Nitrotoluene	67.9	64.3	0	0	0	0
3	m-Nitrotoluene	62.2	59.1	0	0	29.7	25.8
4	p-Nitrotoluene	65.9	62.2	0	0	50.5	42.5
5	1-Chloro-3-nitrobenzene	63.0	61.5	0	0	18.1	15.7
6	1-Chloro-4-nitrobenzene	64.9	64.0	0	0	26.1	23.3
7	1-Chloro-2-nitrobenzene	67.5	67.2	0	0	24.1	21.3
8	2-Chloro-6-nitrotoluene	67.6	66.5	0	0	27.6	24.5
9	4-Chloro-2-nitrotoluene	69.5	68.5	0	0	37.3	33.6
10	3,5-Dichloronitrobenzene	66.3	66.7	0	0	40.7	37.0
11	2,5-Dichloronitrobenzene	71.7	71.5	0	0	40.1	36.1
12	2,4-Dichloronitrobenzene	75.6	75.8	0	0	53.6	48.8
13	4-Chloro-3-nitrotoluene	79.5	76.4	0	0	58.4	53.9
14	3,4-Dichloronitrobenzene	76.3	77.0	0	0	59.1	53.6
15	2,3-Dichloronitrobenzene	78.1	78.5	0	0	58.9	53.6
16	2,4,6-Trichloronitrobenzene	66.8	66.4	0	0	55.7	51.3
17	1,4-Naphthoquinone	74.6	76.3	0	0	42.8	38.5
18	1,2,4-Trichloro-5-nitrobenzene	78.8	79.6	0	0	71.4	65.5
19	1,4-Dinitrobenzene	62.1	62.2	0	0	61.7	58.2
20	2,6-Dinitrotoluene	77.8	79.5	1.8	0	79.6	73.5
21	1,3-Dinitrobenzene	66.6	68.5	0	0	68.0	63.3
22	1,2,3-Trichloro-4-nitrobenzene	80.2	80.7	0	0	75.8	69.8
23	2,3,5,6-Tetrachloronitrobenzene	78.2	80.3	0	0	68.4	62.7
24	1,2-Dinitrobenzene	67.6	69.7	0	0	63.0	58.9
25	2,4-Dinitrotoluene	68.3	68.4	0	0	59.6	58.0
26	1-Chloro-2,4-dinitrobenzene	78.7	79.3	0	0	79.0	73.5
27	2,3,4,5-Tetrachloronitrobenzene	83.2	84.0	0	0	84.4	77.9
28	1-Chloro-3,4-dinitrobenzene	75.7	76.1	0	0	76.9	71.0
29	Trifluralin	85.2	86.5	0	0	86.2	79.2
30	Benefin	85.4	86.5	0	0	89.5	81.7
31	Pentachloronitrobenzene	82.7	84.8	0	0	82.0	76.0
32	Profluralin	90.7	90.5	0	0	90.2	83.5
33	Dinitramine	84.1	85.1	0	0	87.3	80.9
34	Butralin	85.9	86.4	0	0	91.1	83.1
35	Isopropalin	86.6	85.8	0	0	89.5	82.7
36	Penoxalin	70.1	71.3	5.4	0	72.3	70.1

[a] The spiking level is 600 ng/g per compound. Experiments 1 and 2 are identical samples (2.5 g spiked sand) extracted in parallel at 150 atm (50°C) 10 min dynamic followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/30 min dynamic for Fractions 1 and 300 atm/70°C/30 min dynamic for Fraction 2. Experiments 3 and 4 are also identical samples (2.5 g sand) extracted in parallel at 300 atm/70°C/60 min dynamic.

1. Nitrobenzene
2. o-Nitrotoluene
3. m-Nitrotoluene
4. p-Nitrotoluene
5. 1-Chloro-3-nitrobenzene
6. 1-Chloro-4-nitrobenzene
7. 1-Chloro-2-nitrobenzene
8. 2-Chloro-6-nitrotoluene
9. 4-Chloro-2-nitrotoluene
10. 3,5-Dichloronitrobenzene
11. 2,5-Dichloronitrobenzene
12. 2,4-Dichloronitrobenzene
13. 4-Chloro-3-nitrotoluene
14. 3,4-Dichloronitrobenzene
15. 2,3-Dichloronitrobenzene
16. 2,4,6-Trichloronitrobenzene
17. 1,4-Naphthoquinone
18. 1,2,4-Trichloro-5-nitrobenzene

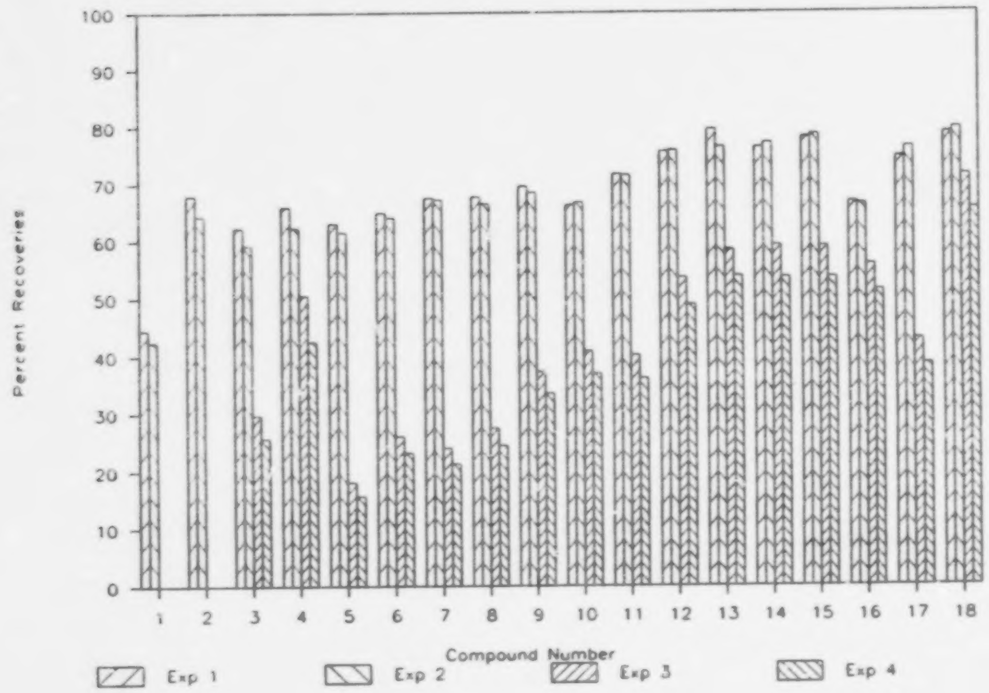


Figure 51. Percent recoveries of 18 nitroaromatics (Compounds 1 through 18) extracted from spiked sand (2.5 g). The experimental conditions are given in the Experimental Section.

19. 1,4-Dinitrobenzene
20. 2,6-Dinitrotoluene
21. 1,3-Dinitrobenzene
22. 1,2,3-Trichloro-4-nitrobenzene
23. 2,3,5,6-Tetrachloronitrobenzene
24. 1,2-Dinitrobenzene
25. 2,4-Dinitrotoluene
26. 1-Chloro-2,4-dinitrobenzene
27. 2,3,4,5-Tetrachloronitrobenzene
28. 1-Chloro-3,4-dinitrobenzene
29. Trifluralin
30. Benfin
31. Pentachloronitrobenzene
32. Profluralin
33. Dinitramine
34. Butralin
35. Isopropalin
36. Penoxalin

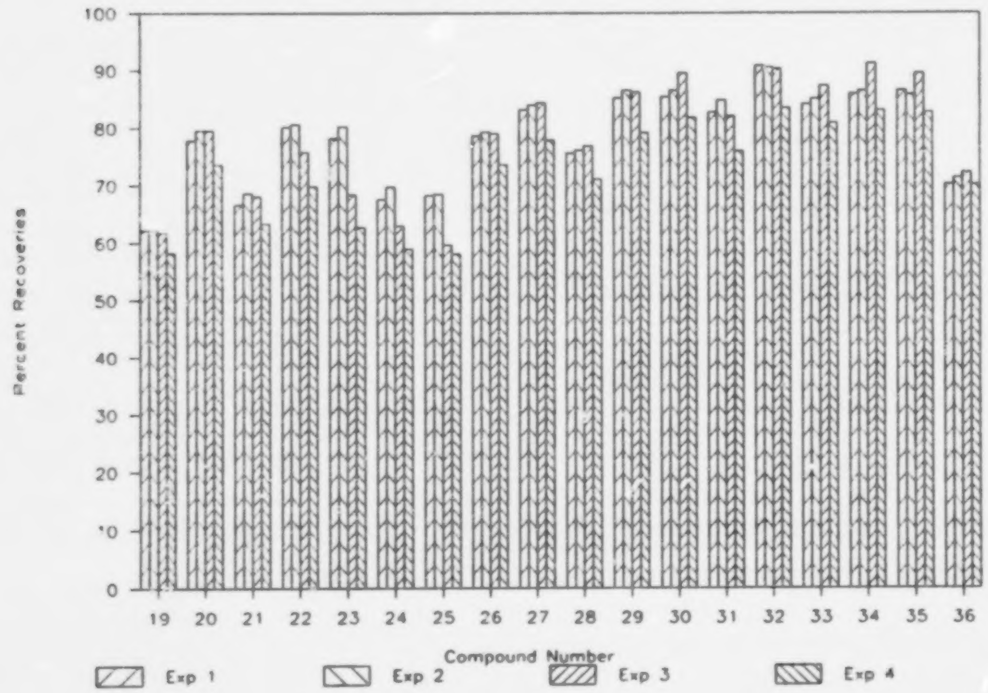


Figure 52. Percent recoveries of additional 18 nitroaromatics (Compounds 19 through 36) extracted from spiked sand (2.5 g). The experimental conditions are given in the Experimental Section.

TABLE 45. PERCENT RECOVERIES OF HALOETHERS FROM SPIKE SAND

Compound no.	Compound	Percent recovery							
		Exp. 1[a]	Exp. 2[a]	Exp. 3[b]	Exp. 4[b]	Exp. 5[c]	Exp. 6[c]	Exp. 7[d]	Exp. 8[d]
1	4-Bromophenyl-phenyl ether	95.3	84.2	63.5	58.0	90.3	99.7	70.8	78.1
2	Phenyl-4'-nitrophenyl ether	88.5	78.0	55.2	59.8	72.6	91.0	69.2	78.6
3	2-Chlorophenyl-4'-nitrophenyl ether	89.5	78.2	62.3	68.1	77.1	89.1	70.4	75.9
4	3-Chlorophenyl-4'-nitrophenyl ether	86.7	75.3	55.8	61.1	71.0	85.0	69.7	76.6
5	4-Chlorophenyl-4'-nitrophenyl ether	89.5	78.4	46.3	56.1	66.5	89.3	60.8	74.3
6	2,6-Dichlorophenyl-4'-nitrophenyl ether	88.2	76.3	60.8	66.5	76.5	89.2	70.0	75.6
7	3,5-Dichlorophenyl-4'-nitrophenyl ether[e]	87.1	75.8	60.6	61.0	69.5	82.9	74.0	78.3
8	2,5-Dichlorophenyl-4'-nitrophenyl ether[e]	87.1	75.8	60.6	61.0	69.5	82.9	74.0	78.3
9	2,4-Dichlorophenyl-4'-nitrophenyl ether	88.9	76.9	55.4	62.7	71.0	85.6	66.6	80.0
10	2,3-Dichlorophenyl-4'-nitrophenyl ether	88.7	75.9	50.0	57.9	60.1	102	63.1	72.0
11	3,4-Dichlorophenyl-4'-nitrophenyl ether	86.6	75.7	50.6	61.0	51.8	84.1	64.9	84.3
12	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	86.8	74.4	59.5	66.1	75.6	90.3	74.1	79.6
13	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	86.3	76.5	66.0	71.5	91.0	107	70.9	72.6
14	2,3,5-Trichlorophenyl-4'-nitrophenyl ether	88.6	77.7	59.9	71.5	91.0	107	76.9	79.3
15	2,4,5-Trichlorophenyl-4'-nitrophenyl ether	85.1	72.9	52.4	60.8	62.2	85.2	63.8	70.7
16	2,4-Dibromophenyl-4'-nitrophenyl ether	86.1	70.7	57.1	56.3	69.8	82.1	58.1	68.4
17	3,4,5-Trichlorophenyl-4'-nitrophenyl ether	83.9	72.1	57.1	61.4	67.9	84.1	64.8	69.4
18	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	83.6	72.2	43.3	55.0	73.5	77.2	57.6	68.3
19	2,4-Dichlorophenyl-3'-methyl-4'-nitrophenyl ether	85.6	72.2	57.1	34.1	63.1	65.8	44.3	55.8

[a] Experiments 1 and 2 were performed in parallel to determine losses during carbon dioxide depressurization. The extraction vessels were filled with glass beads and the test compounds were spiked directly into the collection vials.

[b] Experiments 3 and 4 are identical samples (2.5 g sand spiked at 600 ng/g in an aluminum cup) extracted in parallel at 250 atm/70°C/60 min dynamic.

[c] Experiments 5 and 6 are identical samples (2.5 g sand spiked at 600 ng/g directly in the extraction vessel) extracted in parallel at 250 atm/70°C/60 min dynamic.

[d] Experiments 7 and 8 are identical samples (2.5 g sand spiked at 600 ng/g) extracted in parallel at 150 atm/50°C/60 min dynamic.

[e] These compounds coelute on both columns.

1. 4-Bromophenyl-phenyl ether
2. Phenyl-4'-nitrophenyl ether
3. 2-Chlorophenyl-4'-nitrophenyl ether
4. 3-Chlorophenyl-4'-nitrophenyl ether
5. 4-Chlorophenyl-4'-nitrophenyl ether
6. 2,6-Dichlorophenyl-4'-nitrophenyl ether
7. 3,5-Dichlorophenyl-4'-nitrophenyl ether
8. 2,5-Dichlorophenyl-4'-nitrophenyl ether
9. 2,4-Dichlorophenyl-4'-nitrophenyl ether
10. 2,3-Dichlorophenyl-4'-nitrophenyl ether
11. 3,4-Dichlorophenyl-4'-nitrophenyl ether
12. 2,4,6-Trichlorophenyl-4'-nitrophenyl ether
13. 2,3,6-Trichlorophenyl-4'-nitrophenyl ether
14. 2,3,5-Trichlorophenyl-4'-nitrophenyl ether
15. 2,4,5-Trichlorophenyl-4'-nitrophenyl ether
16. 2,4-Dibromophenyl-4'-nitrophenyl ether
17. 3,4,5-Trichlorophenyl-4'-nitrophenyl ether
18. 2,3,4-Trichlorophenyl-4'-nitrophenyl ether
19. 2,4-Dichlorophenyl-3'-methyl-4'-nitrophenyl ether

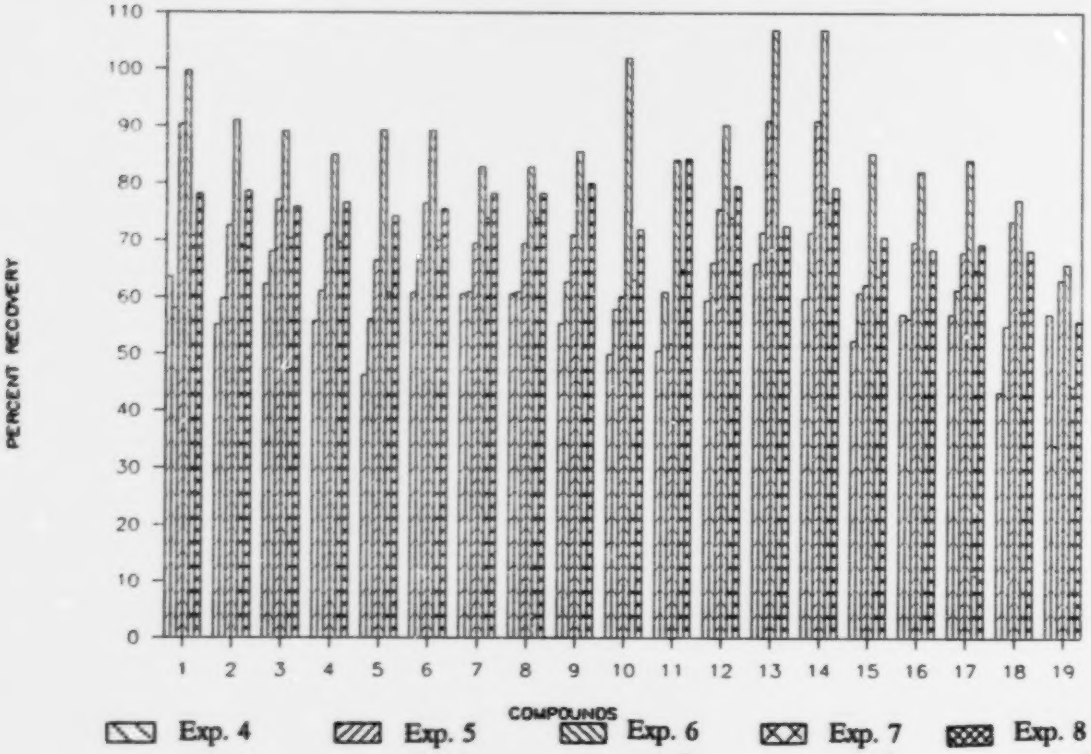


Figure 53. Percent recoveries of 19 haloethers extracted from spiked sand (2.5 g). The experimental conditions are given in the Experimental Section.

TABLE 46. AVERAGE RECOVERIES AND PERCENT RSDs FOR 19 HALOETHERS EXTRACTED FROM SPIKED SAND[a]

Compound no.	Compound	Average recovery	Percent RSD
1	4-Bromophenyl-phenyl ether	93.8	1.2
2	Phenyl-4'-nitrophenyl ether	84.5	3.3
3	2-Chlorophenyl-4'-nitrophenyl ether	66.4	5.8
4	3-Chlorophenyl-4'-nitrophenyl ether	85.5	3.7
5	4-Chlorophenyl-4'-nitrophenyl ether	81.7	6.5
6	2,6-Dichlorophenyl-4'-nitrophenyl ether	85.3	4.6
7	3,5-Dichlorophenyl-4'-nitrophenyl ether	89.4	3.9
8	2,5-Dichlorophenyl-4'-nitrophenyl ether	89.4	3.9
9	2,4-Dichlorophenyl-4'-nitrophenyl ether	80.6	4.1
10	2,3-Dichlorophenyl-4'-nitrophenyl ether	78.8	7.5
11	3,4-Dichlorophenyl-4'-nitrophenyl ether	87.8	8.6
12	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	91.5	1.7
13	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	84.7	11.9
14	2,3,5-Trichlorophenyl-4'-nitrophenyl ether	88.8	2.0
15	2,4,5-Trichlorophenyl-4'-nitrophenyl ether	78.8	3.3
16	2,4-Dibromophenyl-4'-nitrophenyl ether	78.7	7.7
17	3,4,5-Trichlorophenyl-4'-nitrophenyl ether	59.2	29.2
18	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	74.0	10.2
19	2,4-Dichlorophenyl-3'-methyl-4'-nitrophenyl ether	46.2	35.6

[a] The number of samples extracted in parallel was 4. The spiking level was 600 ng/g. The experiments were performed with supercritical carbon dioxide at 250 atm/60°C/60 min dynamic. The sample size was 2.5 g spiked sand.

TABLE 47. AVERAGE RECOVERIES AND PERCENT RSDs FOR 42 ORGANOCHLORINE PESTICIDES FROM SPIKED SAND[a]

Compound no.	Compound	Spike level (ng/g)	Average recovery	Percent RSD
1	DBCP	62.5	7.0	30.8
2	Hexachlorocyclopentadiene	62.5	22.6	10.4
3	Etridiazole	62.5	76.8	4.5
4	Chloroneb	1250	85.2	4.1
5	Propachlor	1250	56.8	11.1
6	Hexachlorobenzene	62.5	73.5	5.3
7	Trifluralin	125	86.7	4.7
8	Diallate	1875	89.2	4.5
9	alpha-BHC	62.5	79.4	5.4
10	PCNB	62.5	75.1	13.2
11	gamma-BHC	62.5	80.8	6.9
12	Heptachlor	62.5	82.2	5.2
13	Chlorthalonil	125	49.0	10.3
14	Alachlor	62.5	65.1	10.1
15	Aldrin	62.5	82.5	5.1
16	beta-BHC	62.5	77.4	5.4
17	delta-BHC	62.5	87.3	4.8
18	DCPA	62.5	77.8	6.8
19	Isodrin	62.5	107	4.3
20	trans-Permethrin	625	69.1	22.6
21	Heptachlor epoxide	62.5	90.2	11.6
22	Endosulfan I	62.5	84.1	4.7
23	gamma-Chlordane	62.5	86.1	5.2
24	alpha-Chlordane	62.5	85.5	4.6
25	trans-Nonachlor	62.5	85.4	4.3
26	p,p'-DDE	62.5	89.1	20.7
27	Captan	125	45.8	7.6
28	Dieldrin	62.5	88.6	3.1
29	Perthane	1875	78.1	5.4
30	Chlorobenzilate	125	0	--
31	Endrin	62.5	83.3	5.0
32	Chloropropylate	62.5	72.5	5.5
33	p,p'-DDD	125	83.3	10.5
34	Endosulfan II	62.5	74.2	14.2
35	p,p'-DDT	62.5	74.0	15.3
36	Endrin aldehyde	125	75.9	3.7
37	Endosulfan sulfate	62.5	0	--
38	Kepone	62.5	64.9	6.1
39	Mirex	125	86.1	4.8
40	Methoxychlor	62.5	60.7	20.4
41	Captafol	62.5	36.2	19.4
42	Endrin ketone	62.5	70.1	6.1

[a] The number of samples extracted in parallel was 4. The experiments were performed with supercritical carbon dioxide at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic. The sample size was 3 g spiked sand.

TABLE 48. AVERAGE RECOVERIES AND PERCENT RSDs FOR 46 ORGANOPHOSPHORUS PESTICIDES FROM SPIKED SAND[a]

Compound no.	Compound	Trial 1		Trial 2		Trial 3	
		Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD
1	Dichlorvos	37.0	13.1	28.0	23.6	30.4	6.9
2	Mevinphos	8.0	24.5	6.8	65.0	7.2	55.7
3	Ethoprop	45.6	14.6	37.1	17.9	38.2	2.7
4	Naled	4.5	17.7	4.7	18.6	6.4	7.7
5	Sulfotepp	75.3	3.9	63.9	15.4	65.7	4.9
6	Phorate	78.9	2.9	65.6	15.5	67.9	5.6
7	Dimethoate	6.0	23.9	4.1	28.4	5.0	5.2
8	Diazinon	5.0	70.5	4.2	39.1	4.3	18.9
9	Disulfoton	65.6	2.2	53.7	16.1	57.2	5.5
10	Parathion methyl	49.0	10.9	43.7	2.9	36.8	22.9
11	Ronnel	79.9	4.8	68.9	22.6	73.2	8.1
12	Malathion	52.3	12.6	41.1	19.8	42.9	3.4
13	Fenthion	66.4	5.8	65.3	3.7	54.8	19.6
14	Chlorpyrifos	75.8	4.8	65.2	20.7	70.4	7.3
15	Parathion ethyl	61.5	7.4	57.4	3.5	47.8	22.0
16	Stirophos	23.5	21.3	17.0	24.5	19.7	2.5
17	Fensulfothion	0	--	0	--	0	--
18	Bolstar	68.6	3.8	57.1	19.9	61.9	5.9
19	EPN	58.6	8.7	47.2	17.0	52.5	8.1

(Continued)

[a] The number of samples extracted in parallel in each trial run was 4. The experiments were performed with supercritical carbon dioxide at 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/10 min dynamic (Trial 1), 200 atm/60°C/30 min dynamic (Trial 2), and 250 atm/70°C/30 min dynamic (Trial 3). The sample size was 2.5 g, the spiking level was 2.5 µg/g.

TABLE 48. (Continued)[a]

Compound no.	Compound	Trial 1 Average recovery	Trial 1 Percent RSD	Trial 2 Average recovery	Trial 2 Percent RSD	Trial 3 Average recovery	Trial 3 Percent RSD
20	Azinphos methyl	0	--	0	--	0	--
21	Coumaphos	7.5	35.5	5.3	22.0	6.2	7.0
22	Demeton-S	60.8	4.1	46.4	19.7	53.9	4.6
23	Merphos	14.3	12.3	19.7	16.4	25.7	12.0
24	Ethion	77.1	4.8	61.5	17.6	66.7	7.5
25	Trimethyl phosphate	18.9	24.6	12.0	29.1	13.4	12.4
26	Hexamethyl phosphoramide	3.0	39.0	1.0	72.2	1.3	6.8
27	Trichlorfon	9.2	14.5	6.4	28.2	5.3	25.9
28	TEPP	0	--	0	--	0	--
29	Thionazin	64.1	8.0	52.1	19.2	54.5	4.3
30	Monocrotophos	0	--	0	--	0	--
31	Terbufos	85.3	4.4	71.9	13.6	72.7	5.0
32	Tricresyl phosphate	85.3	4.4	71.9	13.6	72.7	5.0
33	Fonophos	80.3	4.7	68.3	15.1	70.5	5.2
34	Dichlorphenthion	74.0	2.0	70.0	2.1	61.6	19.9
35	Phosphamidon	61.9	3.6	54.5	19.4	56.7	7.5
36	Methyl chlorpyrifos	72.9	5.3	62.1	21.7	67.6	7.5
37	Fenithrothion	62.5	8.8	50.2	21.2	57.4	9.5

(Continued)

[a] The number of samples extracted in parallel in each trial run was 4. The experiments were performed with supercritical carbon dioxide at 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/10 min dynamic (Trial 1), 200 atm/60°C/30 min dynamic (Trial 2), and 250 atm/70°C/30 min dynamic (Trial 3). The sample size was 2.5 g, the spiking level was 2.5 µg/g.

TABLE 48. (Concluded)[a]

Compound no.	Compound	Trial 1		Trial 2		Trial 3	
		Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD
38	Aspon	75.3	4.4	65.3	16.7	67.9	5.8
39	Trichloronate	78.8	3.1	69.6	21.4	73.3	8.1
40	Chlorfenvinphos	18.3	22.8	13.8	22.9	16.3	3.6
41	Crotoxyphos	5.1	35.6	0	--	4.4	8.2
42	Tokuthion	80.3	3.6	69.8	21.1	73.0	7.8
43	Famphur	0	--	0	--	0	--
44	Phosmet	8.8	36.6	6.1	19.5	7.5	3.5
45	Leptophos	78.7	3.3	64.8	24.2	70.4	8.1
46	Azinphos ethyl	6.8	49.9	5.7	58.5	7.7	47.7

[a] The number of samples extracted in parallel in each trial run was 4. The experiments were performed with supercritical carbon dioxide at 150 atm/50°C/10 min static, 200 atm/60°C/10 min dynamic, 250 atm/70°C/10 min dynamic (Trial 1), 200 atm/60°C/30 min dynamic (Trial 2), and 250 atm/70°C/30 min dynamic (Trial 3). The sample size was 2.5 g, the spiking level was 2.5 µg/g.

TABLE 49. AVERAGE RECOVERIES AND PERCENT RSDs FOR 30 TARGET ANALYTES SPIKED ON DIFFERENT MATRICES[a]

		Sand		Clay		Topsoil		Organic compost mixed with sand	
Compound no.	Compound	Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD
1	1,3-Dichlorobenzene	0	–	0	–	0	–	93.6	29.2
2	1,2-Dichlorobenzene	0	–	0	–	0	–	79.5	24.3
3	Nitrobenzene	0	–	0	–	53.6	32.9	76.6	22.7
4	Benzal chloride	0	–	0	–	30.1	36.3	81.6	24.6
5	Benzotrichloride	0	–	0	–	0	–	80.3	27.1
6	4-Chloro-2-nitrotoluene	56.9	25.9	57.8	28.9	68.3	24.4	86.4	24.5
7	Hexachlorocyclopentadiene	16.9	11.8	15.1	60.1	47.4	33.1	81.8	23.6
8	2,4-Dichloronitrobenzene	57.8	16.1	62.3	27.9	68.9	24.2	73.4	22.9
9	3,4-Dichloronitrobenzene	68.7	30.1	62.9	25.6	69.9	23.4	76.0	18.9
10	Pentachlorobenzene	60.9	16.8	50.9	21.8	68.3	20.1	84.0	24.0
11	2,3,4,5-Tetrachloronitrobenzene	75.3	15.1	65.8	26.3	74.2	19.1	73.9	20.5
12	Benefin	70.4	9.5	65.9	27.8	76.0	18.7	73.9	21.9
13	alpha-BHC	72.5	13.6	66.1	31.3	75.3	18.7	75.3	22.7
14	Hexachlorobenzene	60.6	10.2	56.7	28.1	73.5	18.2	74.1	21.9
15	delta-BHC	68.7	2.8	73.8	25.8	81.3	14.7	81.7	21.7
16	Heptachlor	82.9	12.5	63.4	28.6	74.9	17.6	87.7	20.9
17	Aldrin	76.9	19.2	62.0	37.8	75.3	19.3	77.5	19.5
18	Isopropalin	111.7	11.8	70.8	26.0	76.9	16.8	81.1	17.9
19	Heptachlor epoxide	79.6	11.6	70.7	27.1	79.4	18.7	81.9	19.6
20	trans-Chlordane	71.0	4.3	71.1	28.2	80.4	17.3	80.4	21.3
21	Endosulfan I	76.7	32.2	68.9	24.3	79.2	15.7	78.3	16.2
22	Dieldrin	82.9	29.5	114.4	21.1	84.5	15.8	82.3	19.6
23	2,5-Dichlorophenyl-4'-nitrophenyl ether	66.9	2.5	74.3	25.2	79.3	16.0	80.6	19.7
24	Endrin	68.5	27.8	76.4	24.7	79.7	15.8	83.9	18.8
25	Endosulfan II	62.8	26.2	76.7	26.5	76.9	13.8	82.8	22.8
26	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	81.6	9.9	76.6	23.3	78.9	14.9	88.3	15.4
27	p,p'-DDT	71.1	15.6	86.9	19.7	82.6	15.6	84.7	12.7
28	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	71.3	3.5	72.9	22.5	79.1	18.2	79.1	17.9
29	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	56.7	22.6	68.7	27.3	68.9	18.6	75.7	19.1
30	Mirex	81.1	30.3	67.3	27.6	79.0	16.4	78.2	20.2

[a] The number of samples extracted in parallel in each trial run was 4. The experiments were performed with supercritical carbon dioxide at 300 atm/70°C/60 min dynamic. The sample size was 4 g.

because these values contain not only errors due to extraction but also errors associated with matrix spiking, transfer of sample extracts to autosampler, extract injection, peak quantitation, etc.

The results presented in Table 47 for the 42 organochlorine pesticides indicate that SFE with carbon dioxide works well for 35 of the 42 compounds (recovery > 50 percent). Among the 35 compounds for which the SFE recoveries were > 50 percent, one compound was at 56.8 percent, four compounds had recoveries from 60 to 70 percent, and 30 compounds had recoveries > 70 percent. Among the seven compounds for which the SFE technique did not give encouraging results were two very volatile compounds (DBCP and hexachlorocyclopentadiene). Three of the remaining five compounds (chlorthalonil, captan, and endosulfan sulfate) were probably too polar and could not be recovered with carbon dioxide; however, we had recovered them quantitatively with carbon dioxide with 10 percent methanol (Table 8). Chlorobenzilate recoveries were poor even when we used carbon dioxide with 10 percent methanol, and captafol was not tested with carbon dioxide with 10 percent methanol. Overall, the reproducibilities (percent RSDs) of the four-extraction-vessel setup for the 42 organochlorine pesticides were better than those for the one-extraction-vessel setup. For example, the RSDs ranged from 3.1 to 30.8 percent (with 25 compounds having RSDs under 10 percent) for the four-extraction-vessel setup and from 2.4 to 29.2 percent (with only 12 compounds having RSDs under 10 percent) for the one-extraction-vessel setup (Table 8).

The results presented in Table 48 for the 46 organophosphorus pesticides indicate both lower recoveries (only 20 of the 46 compounds had recoveries > 50 percent in all three trial experiments) and higher RSDs, especially for compounds with low recoveries. We reported previously (16) that significant improvement in recoveries was achieved by extracting with carbon dioxide with 10 percent methanol, although compounds such as phorate and demeton-S appeared to have hydrolyzed in the presence of methanol.

The results presented in Table 49 for the 30 target analytes representing chlorinated hydrocarbons, nitroaromatics, organochlorine pesticides, and haloethers indicate that, with the exception of compounds 1 through 5 and compound 7, the extraction efficiencies are quite good and fairly reproducible when using the four-extraction vessel setup. It is interesting to note that the recovery data for compounds 1 through 5 and compound 7 are very high for the matrix capacity of organic compost mixed with sand, suggesting that these compounds are probably adsorbed to the organic material in the matrix, and that they take much longer to be extracted from the matrix into the collection vessel. Nonetheless, they do get extracted from this matrix within 60 min time, as indicated by their high recoveries. On the other hand, when these compounds are spiked on sand or clay, they are probably removed immediately by the supercritical carbon dioxide and subsequently lost from the collection vessel through volatilization.

Standard Reference Material

One standard reference material SRS 103-100, certified for 13 PAHs, dibenzofuran, and pentachlorophenol was extracted with carbon dioxide. The results are presented in Table 50. This soil is certified for 15 compounds at concentrations ranging from 19.1 to 1618 mg/kg. The values given in Table 50 are for two trial experiments in which we collected two fractions per sample; they indicate clearly that a 30-min extraction will not completely remove the target analytes from the matrix. Even after 60 min, the recoveries of benzo(a)anthracene, chrysene, benzo(b+k)fluoranthene, and benzo(a)pyrene were still below 40 percent (in Fractions 1 and 2 combined). The percent RSDs for Fraction 1 were higher than those obtained for the spiked

TABLE 50. AVERAGE RECOVERIES AND PERCENT RSDs FOR 15 TARGET ANALYTES EXTRACTED FROM SRS 103-100 WITH SUPERCRITICAL CARBON DIOXIDE (FRACTION 1)[a]

Compound	Certified value (mg/kg)	Fraction 1				Fraction 2			
		Trial 1		Trial 2		Trial 1		Trial 2	
		Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD	Average recovery	Percent RSD
Naphthalene	32.4 ± 8.2	54.0	11.6	56.9	12.8	0	--	13.5	23.5
2-Methylnaphthalene	62.1 ± 11.5	79.0	11.9	66.4	4.9	5.9	28.2	17.1	42.9
Acenaphthylene	19.1 ± 4.4	52.4	10.2	44.2	28.1	0	--	13.1	19.8
Acenaphthene	632 ± 105	96.3	10.2	75.9	15.0	9.7	17.2	19.4	24.5
Dibenzofuran	307 ± 49	105	9.9	80.6	14.3	9.8	23.5	19.9	26.9
Fluorene	492 ± 78	81.2	12.3	63.2	13.4	10.4	21.4	18.9	15.1
Phenanthrene	1618 ± 348	92.1	23.4	72.1	17.1	21.0	18.4	34.0	24.0
Anthracene	422 ± 49	79.4	17.2	62.0	23.4	16.7	26.6	24.7	14.8
Fluoranthene	1280 ± 220	73.1	29.1	52.0	28.6	16.0	15.4	26.0	26.2
Pyrene	1033 ± 289	48.3	23.1	44.7	36.2	16.2	8.8	27.1	22.4
Benzo(a)anthracene	252 ± 38	32.4	22.2	27.8	34.5	11.6	7.8	19.2	27.9
Chrysene	297 ± 26	31.1	21.7	27.6	31.2	10.2	6.0	19.0	29.2
Benzo(b+k)fluoranthene	152 ± 22	0	--	0	--	7.3	11.7	12.3	45.9
Benzo(a)pyrene	97.2 ± 17.1	0	--	0	--	4.5	24.4	9.3	79.8
Pentachlorophenol	965 ± 374	52.1	23.7	52.3	34.2	14.8	16.9	31.3	29.8

[a] The number of samples extracted in parallel in each trial run was 4. The experiments were performed with supercritical carbon dioxide at 300 atm/70°C/30 min (Fraction 1) and 350 atm/70°C/30 min (Fraction 2). The sample size was 2.5 g.

sand (ranges were from 9.9 to 23.7 percent for Trial 1 and from 4.9 to 36.2 percent for Trial 2). The percent RSDs for Fraction 2 were higher than those obtained for Fraction 1 (ranges were from 6.0 to 28.2 for Trial 1 and from 14.8 to 79.8 for Trial 2).

The only limitation that we have experienced with the four-extraction vessel setup was in the duration of the extraction. When working with 2-mL extraction vessels and using 50-μm restrictors, the 250-mL syringe pump allows us a maximum extraction time of 60 min. During this time, two 30-min fractions can be collected with the present setup.

5.4 COST CONSIDERATIONS

When new methodologies are introduced, method performance is usually the determining factor in the decision-making process. However, the costs associated with setting up the equipment and with implementing and using an analytical method play a very important role in determining whether or not a laboratory can profitably use a particular methodology.

It has been claimed that the costs of performing extractions by SFE are not more than about $1. However, this price tag seems to comprise only the cost of the supercritical fluid (carbon dioxide) for small samples (smaller than 1 g). To get a more realistic picture of the actual expenditures for performing extractions by SFE, one also needs to consider the costs associated with the hardware (SFE system purchase, replacement of extraction vessels, frits, nuts, valves, restrictors, ferrules, etc.) and of the manpower required. To get an estimate of the capital investment needed to set up a laboratory for the SFE technique, we have compiled in Table 51 a list of the parts and equipment which we actually needed during the last year in order to perform extractions by SFE. When the cost of purchasing the SFE system and necessary parts are prorated, and when the assumption is made that a chemist will have to spend on the average one hour for each sample, then the cost of extracting a sample by SFE amounts to about $60 per sample. To allow comparison of the SFE costs with those of conventional extractions, we included in Table 51 the costs of purchasing 10 Soxhlet extractors and the associated glassware, heating mantles, Kuderna-Danish equipment, etc. We made the assumption that in order to extract 100 samples, a laboratory will have to set up 10 Soxhlet extractors and have 5 Kuderna-Danish evaporators ready for solvent concentration. If these 10 extractors and the 5 evaporator systems have to be replaced every 1,000 samples due to breakage, then the equipment cost per sample is approximately $4. To perform 100 extractions, a chemist will spend on the average 90 hrs at a cost of approximately $11 per sample. In addition to these costs, we included the costs associated with waste solvent disposal (at $5 per sample) and glassware cleaning (at $3 per sample). Thus, the cost of performing an extraction by Soxhlet would be about $23 per sample.

However, SFE is a new technique, and the cost per analysis will significantly decrease when the technique has been optimized and when replacement parts are used and available on a larger scale. Furthermore, as we have shown in Section 5.3 in this report, multiple parallel extractions are feasible, and when a four-vessel-extraction setup can be used, the extraction cost per sample can easily be lowered to the cost of a Soxhlet extraction.

TABLE 51. COST CONSIDERATIONS--SFE VERSUS CONVENTIONAL SOXHLET EXTRACTION

SFE				Soxhlet extraction			
Component	Full cost ($)	Number of extractions performed	Cost per sample ($)	Component	Full cost ($)	Number of extractions performed	Cost per sample ($)
Extraction vessel	410	300	1.35	Soxhlet (10)	960.00		
Fused-silica restrictor	10/m	2	5.00	Condenser (10)	700.00		
Internal reducer	20	20	1.00	Flask (10)	150.00		
Ferrule	5	2	2.50	K-D flask (5)	150.00		
Rotor for 4-port valve	140	140	1.00	Snyder column (5)	212.50		
Valve head	475	300	1.60	Receiver tube (5)	92.50		
Collection vials (2)	1.00	1	1.00	Heating mantle (10)	790.00		
Frits (2)	4.90	1	9.80	Thimbles (25)	40.00		
Stainless steel tubing	5.00	1	5.00	Variacs (2)	232.00		
Valco gland and ferrule (5/set)	5.00	1	5.00	Hexane (20 L) Acetone	105.00 173.00		
Valco 4-port valve	1,800	1,000	1.80	Na_2SO_4	195.00		
Carbon dioxide without or with modifiers			1.00	Total cost	3,800.00	1,000	3.80
Storage charges for carbon dioxide cylinders			0.50				
SFE instrument	15,000-50,000	10,000	1.50-5.00	Chemist time for 100 extractions at $12/hr	90 hrs	100	10.80
Cost			38.05-41.55	Waste disposal			5.00
				Glassware cleaning			3.00
Chemist time + 1 hour/extraction			15.00-20.00				
							22.60
			53.05-61.55				

REFERENCES

1. Test Methods for Evaluating Solid Waste (1986), 3rd Ed., SW-846, U. S. Environmental Protection Agency, Washington, D. C.

2. M. A. McHugh and V. J. Krukonis. "Supercritical Fluid Extraction: Principles and Practice," Butterworth Publishers, 1986.

3. B.O. Brady, C.P.C. Kao, K.M. Dooley, F.C. Knopf, and R.P. Gambrell, "Supercritical Fluid Extraction of Toxic Organics from Soils," Ind. Eng. Chem. Res. 26: 261-268 (1987).

4. M.M. Schantz and S.N. Chesler, "Supercritical Fluid Extraction Procedure for the Removal of Trace Organic Species from Solid Samples," J. Chrom. 363: 397-401 (1986).

5. H.T. Kalinowski, H.R. Udseth, B.W. Wright, and R.D. Smith, "Supercritical Fluid Extraction and Direct Fluid Injection Mass Spectrometry for the Determination of Trichothecene Mycotoxins in Wheat Samples," Anal. Chem. 58: 2421-2429 (1986).

6. R.D. Smith, H.R. Udseth and R.N. Hazlett, "Diesel Fuel Marine and Sediment Analysis: Supercritical Ammonia Extraction and Direct Fluid Injection Mass Spectrometry," Fuel 64: 810-815 (1985).

7. B.W. Wright and R.D. Smith, "Supercritical Fluid Extraction of Particulate and Adsorbent Materials: Part II," EPA Report 600/4-87/040 (1987).

8. B.W. Wright, J.L. Fulton, A.J. Kopriva, and R.D. Smith, "Analytical Supercritical Fluid Extraction and Chromatography: Techniques and Applications," B.A. Charpentier and M.R. Sevenants, Editors. ACS Symposium Series 366: 44-62 (1988).

9. S.B. Hawthorne and D.J. Miller, "Directly Coupled Supercritical Fluid Extraction--Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls from Environmental Solids," J. Chrom. 403: 63-76 (1987).

10. S.B. Hawthorne, M.S. Krieger, and D.J. Miller, "Analysis of Flavor and Fragrance Compounds Using Supercritical Fluid Extraction Coupled with Gas Chromatography," Anal. Chem. 60: 472-477 (1988).

11. S.B. Hawthorne and D.J. Miller, "Extraction and Recovery of Organic Pollutants from Environmental Solids and Tenax-GC Using Supercritical CO_2," J. Chrom. Sci. 24: 258-264 (1986).

12. S.B. Hawthorne and D.J. Miller, "Extraction and Recovery of Polycyclic Aromatic Hydrocarbons from Environmental Solids Using Supercritical Fluids," Anal. Chem. 59: 1705-1708 (1987).

13. V. Janda, G. Steenbeke, and P. Sandra, "Supercritical Fluid Extraction of s-Triazine Herbicides from Sediment," J. Chrom. 479: 200-205 (1989).

14. N. Alexandrou and J. Pawliszyn, "Supercritical Fluid Extraction for the Rapid Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash," Anal. Chem. 61: 2770-2776 (1989).

15. F.I. Onuska and K.A. Terry, "Supercritical Fluid Extraction of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Sediment Samples," J. High Resol. Chrom. 12: 357-361 (1989).

16. J.M. Dobbs, J.M. Wong, R.J. Lahiere, and K.P. Johnston, "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents," Ind. Eng. Chem. Res. 26: 56-65 (1987).

17. K.M. Dooley, C.P.C. Kao, R.P. Gambrell, and F.C. Knopf, "The Use of Entrainers in the Supercritical Extraction of Soils Contaminated with Hazardous Organics," Ind. Eng. Chem. Res. 26: 2058-2062 (1987).

18. W.J. Youden and E.H. Steiner, "Statistical Manual of the Association of the Official Analytical Chemists Statistical Techniques for Collaborative Tests," Association of the Official Analytical Chemists (1975).

APPENDIX A

EXTRACTION OF TRACE ORGANICS FROM SOILS AND SEDIMENTS USING SUPERCRITICAL FLUID EXTRACTION TECHNIQUES

LITERATURE REVIEW

CONTENTS

Section Page

1 **INTRODUCTION** 1

2 **THEORY OF SFE** 3

2.1 PROPERTIES OF SCFs 3
2.2 FACTORS AFFECTING SOLUBILITY IN SCFs 4
2.3 MEASUREMENT OF SOLUBILITIES IN SCFs 16

2.3.1 Dynamic Method 17
2.3.2 Static Method 18

2.4 SFE PROCESS 18

3 **APPARATUS** 23

3.1 OFF-LINE SFE 23
3.2 ULTRASONIC SFE 35
3.3 ON-LINE SFE 35

4 **APPLICATIONS** 44

4.1 MATRIX/SCF/ENTRAINER EFFECTS 44
4.2 EFFECT OF TEMPERATURE/PRESSURE/FLOWRATE 61
4.3 SAMPLE COLLECTION 64

REFERENCES 70

141

SECTION 1

INTRODUCTION

Extraction of solid samples with liquid solvents requires relatively long periods of time to perform, recoveries are often far from quantitative, and the extracted analytes are diluted by relatively large volumes of solvents so that concentrating steps are required. Solvent removal is also a time-consuming process, and analyte losses may result. Furthermore, the use of liquid solvents can be hazardous, and solvents and their disposal are expensive.

Supercritical fluid extraction (SFE) of solid samples is a new and promising technique. Supercritical fluids (SCFs) have low viscosities, zero surface tension, and thus, solute diffusivities in SCFs are much higher than those in liquid solvents. Consequently, extraction efficiencies can be much higher with SCFs than with liquid solvents. Furthermore, extraction or separation of compounds of low volatility can be accomplished at low temperature. This is especially advantageous in the case of thermally labile compounds. The high volatility of SCFs at ambient temperature and pressure permits a virtually complete and easy separation of solvent from solute, and many SCFs are nontoxic. Finally, some mixtures of compounds can be fractionated during SFE, all in one continuous process, which makes the technique very selective.

The purpose of this work assignment is to develop an efficient extraction technique for soil and sediment matrices using SCFs and commercially available SFE systems. The feasibility of on-line SFE and gas chromatography or supercritical fluid chromatography (SFC) will also be addressed.

This report is a review of relevant literature. The literature was gathered using the Chemical Abstracts search and recent issues of scientific journals, including Analytical Chemistry, Fluid Phase Equilibria, Industrial and Engineering Chemical Research, Industrial Engineering Chemical Products Research and Development, Journal of Chromatography, and Separation Science. Furthermore, several books, as well as symposia proceedings devoted to SFE and published either in the form of books or as special volumes of a journal, have been used (1-6). A number of review articles (7-17) have been published from 1970 onwards. These articles describe the progress achieved in the SFE technique, however, little emphasis has been placed on its application to environmental analysis, and many questions regarding experimental conditions (pressure, temperature, sample size, modifier, etc.), instrumentation (extraction vessel design, restrictor design, collection system, etc.), and sample matrix effects were usually not addressed in detail. As is normally the case with any new field, there has been a flow of papers reporting new information, particularly in the late 1980's. These papers (18-134) have also been reviewed.

This literature review summary addresses the following:

- Theory of SFE
- Recent developments in equipment used for SFE
- Applications of SFE.

SECTION 2

THEORY OF SFE

2.1 PROPERTIES OF SCFs

The supercritical state of a gas refers to those conditions of temperature and pressure under which the gas can be compressed to a density which approximates that of a liquid. Above the critical temperature, the gas will not become a liquid regardless of pressure. However, by increasing pressure, the density of the gas will increase. Thus, the characteristics of an SCF are determined by both temperature and pressure. Compounds used or proposed for use as SCFs and their properties are listed in Table 1. The important properties of SCFs are summarized below:

- The compressibility of SCFs above the critical temperature is high, and slight changes in pressure result in large changes in density, and thus, in the ability to solubilize compounds.

TABLE 1. EXAMPLES OF SCFs AND THEIR PROPERTIES

Compound	Boiling point (°C)	Critical temperature (°C)	Critical pressure (atm)	Critical density (g/mL)
Xenon	-107	16.6	57.6	1.100
Carbon dioxide	-78.5	31.3	72.9	0.448
Ammonia	-33.3	132.4	112.5	0.235
Water	100.0	374.1	218.3	0.315
Nitrous oxide	-88.6	36.5	71.7	0.450
Ethane	-88.6	32.3	48.1	0.203
Ethene	103.7	9.2	49.7	0.218
Propane	-42.1	96.7	41.9	0.217
Pentane	36.1	196.6	33.3	0.232
Benzene	80.1	288.9	48.3	0.302
Methanol	64.7	240.5	78.9	0.272
Isopropanol	82.5	235.3	47.0	0.273

- The densities of SCFs are typically 100 to 1,000 times greater than those of gases, however, their viscosities and diffusion coefficients are intermediate between those of liquids and gases, thus, allowing rapid transfer of solutes into the SCF. Consequently, the separation efficiencies for SFEs are higher than those for liquid solvent extractions.

- Many SCFs have low critical temperatures, thus, extractions can be performed at relatively low temperatures (e.g., as low as 31°C for carbon dioxide).

An inspection of the data in Table 1 reveals that:

- The listed hydrocarbons have critical pressures under 50 atm. Methanol, carbon dioxide, and nitrous oxide have critical pressures of 70 to 80 atm, and only the critical pressures for ammonia and water exceed 100 and 200 atm, respectively. The high critical pressures for the last two fluids is a result of their polarities and hydrogen bonding;

- Carbon dioxide has a low critical temperature (31°C) and a relatively low critical pressure (73 atm).

The solubilizing power of an SCF has been related to the fluid density in the critical region. To explain this relationship, we present in Figure 1 the variation in the reduced density (ρ_R) of a pure component in the vicinity of its critical point. For a reduced temperature (T_R) range of 0.9 to 1.2 and at reduced pressures (p_R) greater than 1.0, the reduced density changes from 0.1 (gas-like density) to 2.5 (liquid-like density). Thus, as the reduced densities approach those of liquids, the SCF behaves like a liquid. However, at reduced temperatures of 1.55 the SCF becomes more expanded, and in order to increase its reduced density to values greater than 1, one must increase the reduced pressure to values as high as 10.

Although an SCF has a liquid-like density over much of the range of interest, it exhibits gas-like transport properties of diffusibility and the viscosity (1). Furthermore, the zero surface tension of SCFs allows them to penetrate easily into microporous materials (1). Figures 2 and 3 show the diffusivity and viscosity behavior of carbon dioxide, respectively, as a function of pressure and temperature.

2.2 FACTORS AFFECTING SOLUBILITY IN SCFs

Factors that affect solubility in SCFs include solute physical properties (vapor pressure, polarity, and molecular weight) and the temperature and pressure of the SCF. The effect of temperature on the solubility of a particular analyte in an SCF changes with pressure. At pressures which are close to the critical point, an increase in temperature results in a decrease in compound solubility. However, at high pressures, an increase in temperature causes an increase in solubility.

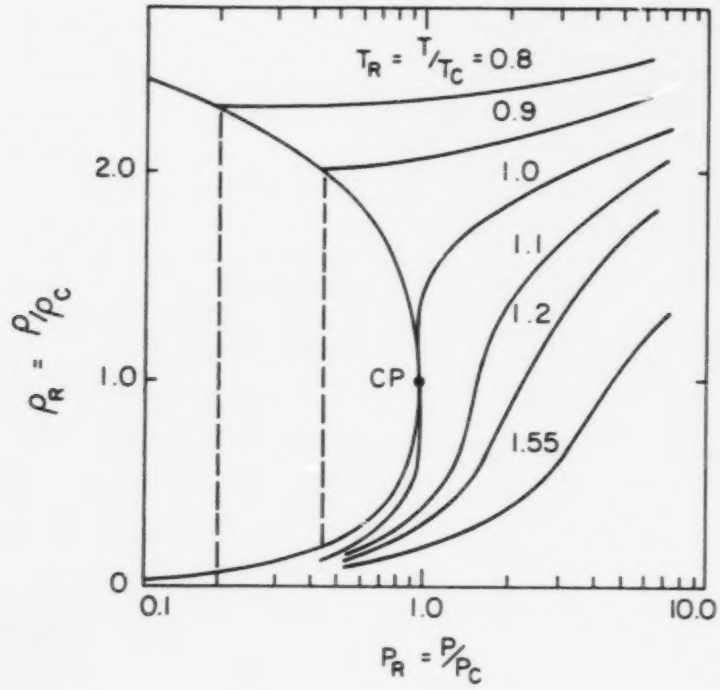


Figure 1. Variation of the reduced density ρ_R of a pure component in the vicinity of its critical point (taken from Reference 1).

147

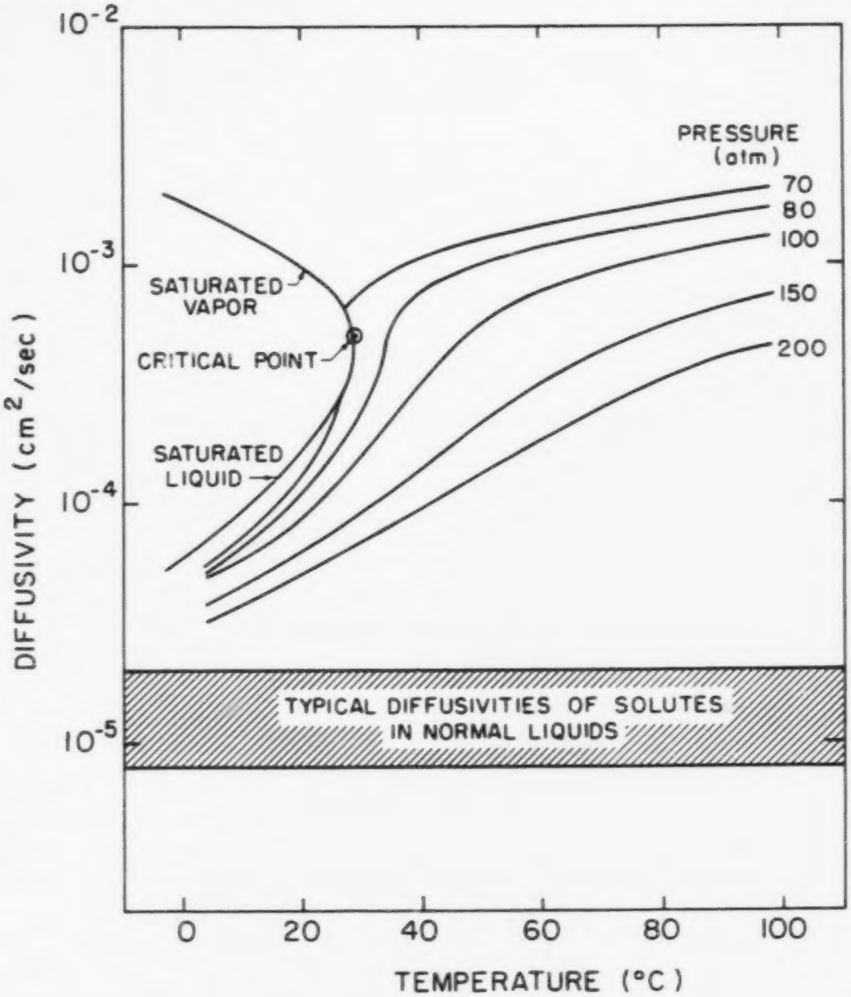


Figure 2. Diffusivity behavior of carbon dioxide (taken from Reference 1).

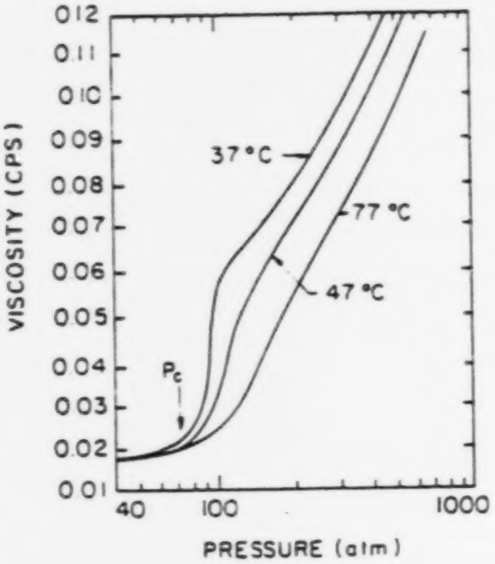


Figure 3. Viscosity behavior of carbon dioxide (taken from Reference 1).

Francis (5) reported the solubilities of 261 compounds in subcritical carbon dioxide (an incomplete list is presented in Table 2). Despite the wealth of data gathered, Francis did not discuss how compound structure affects its solubility in subcritical carbon dioxide. Dandge et al. (33) measured solubilities of other compounds and used their data (Table 3) and Francis' data to identify structural features that either limit or enhance the solubility of different groups of compounds. Here is a summary of Dandge's et al. conclusions (33) regarding structure-solubility correlations:

- For normal alkanes with less than 12 carbon atoms there is complete miscibility with carbon dioxide. As the carbon number increases above 12, the miscibility decreases rapidly. For example, n-dodecane is miscible while n-tetradecane, n-hexadecane, and n-octadecane have solubilities of 16, 8, and 3 percent, respectively.
- Branched alkanes are more soluble than normal alkanes. The maximum limit of complete miscibility is between 19 and 30 carbon atoms as compared to 12 in the case of normal alkanes.

TABLE 2. SOLUBILITIES OF ORGANIC COMPOUNDS IN LIQUID CARBON DIOXIDE[a]

Compound	Solubility (percent)
Aromatic compounds	
Naphthalene	2
Tetralin	12
Decalin	22
Cyclohexylbenzene	8
Biphenyl	2
Diphenylmethane	4
α-Methylnaphthalene	6
β-Methylnaphthalene	9
α-Methoxynaphthalene	1
Methoxybiphenyl	5
α-Chloronaphthalene	1
(Dichloromethyl)benzene	miscible
(Trichloromethyl)benzene	2
Bibenzyl	1
Alcohols	
Furfuryl alcohol	4
β-Chloroethanol	10
Cinnamyl alcohol	5
Cyclohexanol	4
Decyl alcohol	1
Diethylene glycol	1
Dipropylene glycol	2
Glycerol	7
Heptyl alcohol	6.2
2-Ethyl-1-hexanol	17
2,4,4-Trimethyl-1-pentanol	miscible
Benzyl alcohol	8
2-Phenylethanol	3

(continued)

[a] Data are taken from Reference 5. Solubilities were measured at 25°C and 955 psi.

TABLE 2. Continued

Compound	Solubility (percent)
Phenols	
Phenol	3
Anisole	miscible
p-Chlorophenol	8
p-Nitrophenol	1.8
o-Cresol	2
m-Cresol	4
p-Cresol	2
2,4-Dichlorophenol	14
2,6-Dinitrophenol	0.9
2-Chloro-6-phenylphenol	1
p-Ethylphenol	1
Nitroaromatics	
o-Nitrotoluene	miscible
p-Nitrotoluene	20
Nitrobenzene	miscible
2,4-Dinitrochlorobenzene	1
o-Nitrochlorobenzene	21
Nitrogen heterocyclics	
Pyridine	miscible
2-Picoline	miscible
Aromatic amines	
Aniline	3
N,N-Dimethylaniline	miscible
N-Methylaniline	20
N,N-Diethylaniline	17
N-Ethylaniline	13
o-Anisidine	1
o-Chloroaniline	5
N-Ethyl-N-benzylaniline	4
m-Chloroaniline	1
Diphenylamine	1

(continued)

---

[a] Data are taken from Reference 5. Solubilities were measured at 25°C and 955 psi.

TABLE 2. Concluded

Compound	Solubility (percent)
Aldehydes	
Benzaldehyde	<0.05
2-Hydroxybenzaldehyde	<0.05
3-Phenyl-2-propenal	4
3-Phenylpropanal	12
Chloral hydrate	2
Cinnamaldehyde	4
Hydrocinnamaldehyde	17
Amides	
Acetamide	1
Formamide	1
Formanilide	0.5
Ketones	
Benzalacetone	5
Benzophenone	4
Anhydrides	
Benzoic anhydride	3
Maleic anhydride	7.5
Esters	
Benzyl benzoate	10
Butyl phthalate	8
Butyl stearate	3
Ethyl phthalate	10
Chlorinated hydrocarbons	
Bromoform	30
Acids	
Chloroacetic acid	10
α-Chloropropionic acid	26

[a] Data are taken from Reference 5. Solubilities were measured at 25°C and 955 psi.

TABLE 3. SOLUBILITIES OF ORGANIC COMPOUNDS IN CARBON DIOXIDE[a]

Compound	Solubility wt-percent	
	25°C, 2500 psi (subcritical)	32°C, 2500 psi (supercritical)
Benzoic acid	0.4	
Decanoic acid	miscible[b]	miscible
2,6-Dihydroxybenzoic acid	0.03	
2,6-Dinitrophenol	0.9	1.0
2,6-Dinitrotoluene	5.9	
Di(o-xylyl)ethane		17.9
Ethyldodecanoate	miscible	miscible
2-Fluorophenol	miscible	miscible
o-Methoxyphenol		21.1
1,4-Benzenediol	insoluble[c]	insoluble
(Z)-Butenedioic acid	0.04	
2-Methyl-3-hexanol	miscible	miscible
2,2-Dimethylpropanoic acid	miscible	miscible
2-Nitroacetophenone		12.9
2-Nitrobenzaldehyde	miscible	miscible
o-Nitrophenol	miscible	miscible
p-Nitrophenol		0.2
Pyrrole	miscible	miscible
Pyrrolidine		salted out
2,6,10,14-Tetramethylpentadecane	miscible	miscible
2,4,4-Trimethyl-1-pentanol	miscible	miscible

[a] Data are taken from Reference 33.

[b] Miscible is used to represent the phase "miscible in all proportions" in dense carbon dioxide.

[c] Insoluble means that the compound was not detectable; detection limit was approximately 0.05 wt-percent.

- Alkenes behave similarly to normal alkanes except that the solubility of an alkene is higher than that of the corresponding n-alkane. For example, 1-octadecene is 10 percent soluble whereas n-octadecane is only 3 percent soluble.

- For dicyclic compounds, increasing hydrogenation increases solubility. Naphthalene (2 percent) < tetralin (12 percent) < decalin (22 percent). Methyl substitution in the case of dicyclic compounds has a favorable effect (e.g., α- and β-methylnaphthalenes have solubilities of 6 percent and 9 percent, respectively).

- Primary alcohols show a significant decrease in solubility when the carbon chain increases beyond six carbon atoms. Branching, on the other hand, increases their solubility (see 2-ethyl-hexanol and 2,4,4-trimethyl-1-pentanol in Table 2). In the case of short-chain alcohols, solubility is completely altered by either complete or partial etherification. In the case of partial etherification, all but one hydroxyl need to be etherified to achieve complete miscibility. Phenyl-substituted alcohols tend to have lower solubility.

- Ortho-chloro- and -nitro-substituted phenols are completely miscible, whereas the same functional groups in para position produce very little increase in solubility. Methyl substitution of phenols, in general, increases solubility.

- Esterification, in general, enhances the solubility of both aliphatic and aromatic carboxylic acids. The presence of halogens, hydroxy groups, and aromaticity decreases the solubility of carboxylic acids.

- Aliphatic aldehydes are miscible, and phenyl-substitution decreases the solubility of unsaturated aldehydes; benzaldehyde and 2-hydroxybenzaldehyde are insoluble.

- Aromatic nitrocompounds differ widely in their solubility. For example, o-nitrotoluene is miscible while p-nitrotoluene solubility is only 20 percent.

Solubility data for other SCFs (or subcritical fluids) are scarce. Schmitt and Reid (45) measured solubilities of naphthalene, 1,4-naphthoquinone, and acridine in supercritical carbon dioxide, ethane, chlorotrifluoromethane, and fluoroform. The solvents were chosen on the basis of their chemical dissimilarities, although their critical temperatures were almost identical (31.3°C; 32.3°C; 28.8°C; and 26.0°C, respectively). Figures 4 through 6 show that the choice of solvent can significantly affect the equilibrium solubility of a particular solute and that acid-base and solvent-solute association effects appear to play a role in some specific cases.

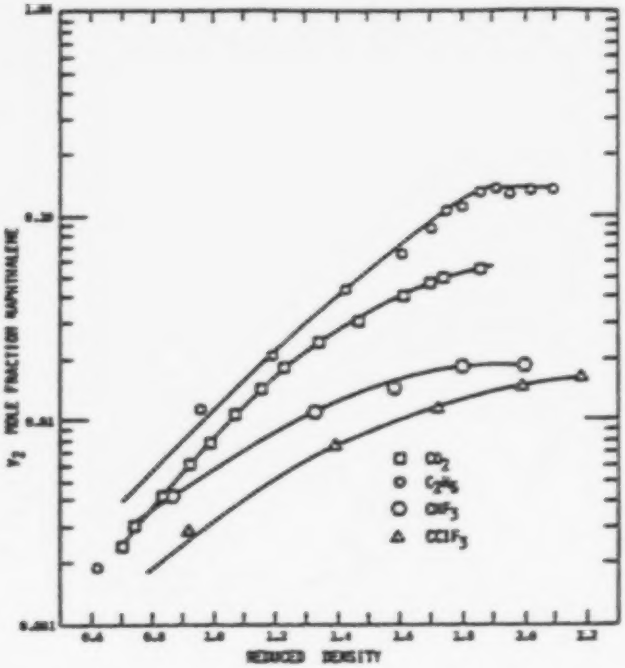


Figure 4. Solubility of naphthalene in four SCFs at 55°C (taken from Reference 45).

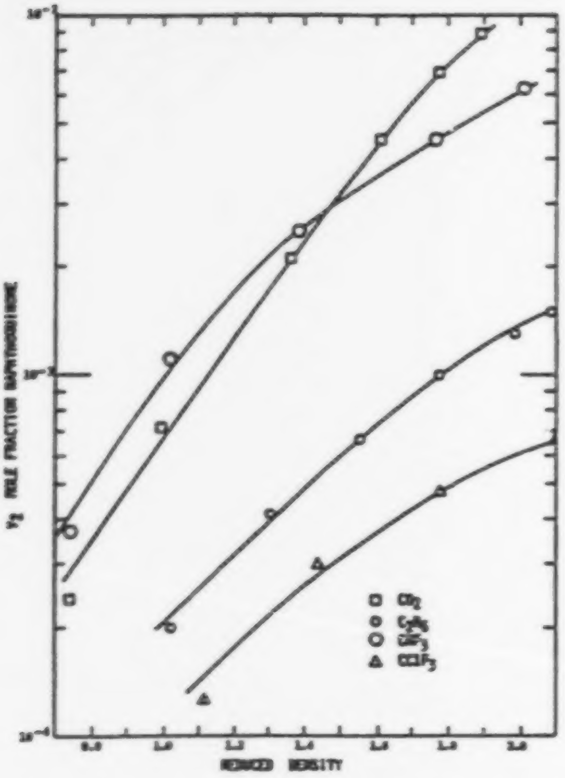


Figure 5. Solubility of 1,4-naphthoquinone in four SCFs at 55°C (taken from Reference 45).

156

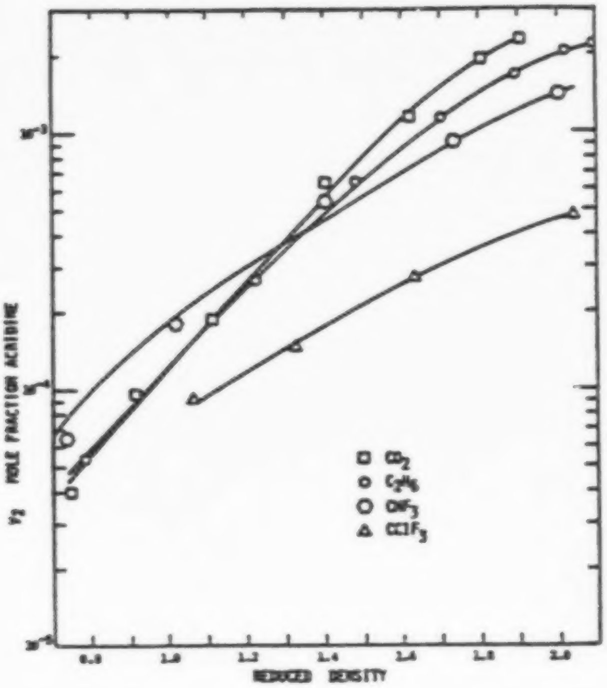


Figure 6. Solubility of acridine in four SCFs at 55°C (taken from Reference 45)

Since the critical temperatures of the four fluids are almost identical and the temperature at which the solubilities were measured was constant, then the reduced temperatures for the four SCFs would be about the same. At constant temperature, the solubilities of the three compounds appear to be strong functions of solvent density. In the case of naphthalene, the highest solubilities were measured in ethane, followed by carbon dioxide, fluoroform, and then chlorotrifluoromethane. Carbon dioxide and fluoroform gave the highest solubilities for 1,4-naphthoquinone. The high solubility in fluoroform was attributed to possible hydrogen bonding between the acidic protons of fluoroform and the carbonyl groups in naphthoquinone. In the case of acridine, carbon dioxide, ethane, and fluoroform were found to be good solvents. The slightly higher solubility of acridine in carbon dioxide was attributed to an acid-base complex which does not form with ethane.

Other sources of solubility data of organic compounds in SCFs are References 14, and 88 through 92.

The effects of entrainers or cosolvents have been explored by Dobbs and Johnston (38). They measured solubilities for binary, ternary, and quaternary systems which consisted of various combinations of solid phases, carbon dioxide, and an entrainer at 35°C and 100 to 350 bar. Solubility-versus-pressure isotherms were obtained for 50:50 mixtures of anthracene/2-aminobenzoic acid, benzoic acid/hexamethylbenzene, and 2-naphthol/anthracene in pure carbon dioxide and in the presence of 3.5 mole percent methanol. For pure solids, the results show that addition of methanol had no effect on the solubility of the least polar compound hexamethylbenzene. In the case of the benzoic acid and 2-aminobenzoic acid, methanol had a definite effect showing a greater increase in solubility for 2-aminobenzoic acid than for benzoic acid. 2-Naphthol also showed an increased in solubility when methanol was added to the supercritical carbon dioxide.

When two compounds are present in a mixture and they are both nonpolar, a cosolvent would cause little change in solubility. If the pair consists of a polar solute and a nonpolar solute, and a polar entrainer is added to carbon dioxide, then a large increase in solubility of the polar solute is expected due to hydrogen bonding between the polar solute and the entrainer. This large increase in solubility is possible for compounds with hydroxy, amino, and carboxyl functional groups. Thus, the use of small amounts of entrainers could impact the economics of certain SFEs due to an increase in selectivity or a reduction in pressure. Additional discussion on the use of SCFs with entrainers is given in Section 4.

2.3 MEASUREMENT OF SOLUBILITIES IN SCFs

A knowledge of the solubility data in SCFs is important to make efficient use of the SFE technique. The methods for measuring solubilities can be either dynamic, in cases where a solute is continually swept with the SCF, or static, in cases where both the solute and the fluid are loaded in a cell.

2.3.1 Dynamic Method

Figure 7 shows a schematic diagram of an apparatus used by Van Leer and Paulaitis (59). The experimental technique is applicable to any SCF but for this discussion the SCF is assumed to be carbon dioxide.

A high-pressure pump is used to continuously deliver carbon dioxide at flow rates slow enough to ensure that equilibrium is obtained between the solute and the carbon dioxide as the carbon dioxide flows through the system. Typical equilibrium-type flow rates are 60-500 cm^3/min of (gaseous) carbon dioxide as determined at 1 atm and 0°C.

The carbon dioxide is first allowed to flow through a section of tubing in the thermostat to reach the desired temperature before it contacts the solute. After thermal equilibrium has been attained, carbon dioxide is fed to the equilibrium cells packed with the solute. The carbon dioxide flows through the cells and gets saturated with the solute prior to exiting the second cell. After the SCF exits the second cell, it is expanded to atmospheric pressure through a metering valve, and the heavy component precipitates and is collected in a cold trap. The amount of solid collected and the flow rate of carbon dioxide are used to calculate solubility.

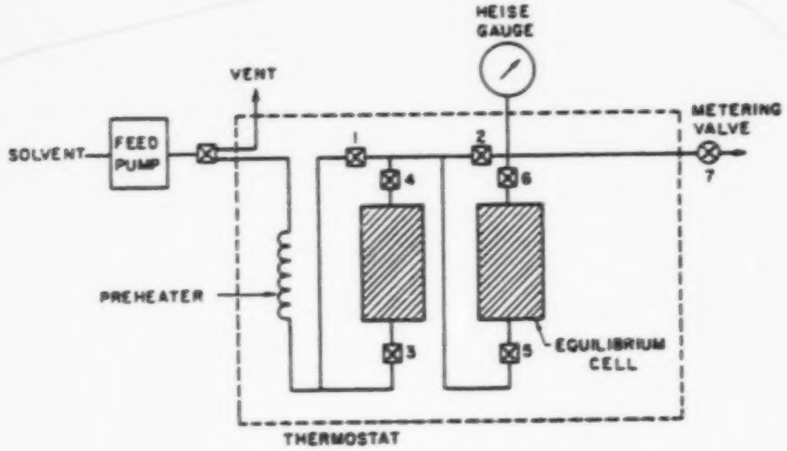


Figure 7. Schematic diagram of a dynamic flow apparatus used to determine solubilities in an SCF (taken from Reference 59).

The advantages of this method are that it is simple and that it can be performed using off-the-shelf equipment. However, there are some disadvantages which need to be identified:

- The metering valve can easily be clogged with solutes which leads to errors in measuring the solubility.
- Some phase changes may take place which go undetected.
- Special care must be given to the design while using this technique with a multicomponent system to avoid complete depletion of one or more components.

The apparatus can be modified to overcome these disadvantages. The simplest modification is to add a sampling valve to the system to obtain a sample of the SCF-rich phase before it flows through the metering valve. McHugh and Paulaitis (60) have described this technique. A schematic diagram is shown in Figure 8. In this method, the contents of the sample loop can be collected and analyzed before the (saturated) carbon dioxide reaches the metering valve.

2.3.2 Static Method

An apparatus used by McHugh, Seckner, and Yogan (61) is shown in Figure 9. In this method, carbon dioxide is charged at ambient temperature to a high-pressure pump, where it is compressed and delivered to a holding tank located in an air bath. The amount of gas in the tank is determined from its density, which is calculated from its pressure, and the volume of the holding tank. The gas is then transferred to the view cell which has been charged previously with a known amount of a solute. The amount of gas transferred is determined by a mass balance based on the density of the gas remaining in the holding tank and the transfer lines, and on the volume of the tank and the lines.

The pressure is isothermally increased until all solute is solubilized in the carbon dioxide. At this point, a clear, single-phase fluid is present in the view cell. The mixture is then slowly decompressed until the solid precipitates from solution, and at this point two phases exist in the view cell. Hence the actual solubility is in the pressure interval between this two-phase state and the previous single-phase state. By repeated measurements, the solubility can be measured to ± 1 percent by this method.

2.4 SFE PROCESS

Figure 10 shows a schematic diagram of a basic SFE process.

For illustration, the extraction of naphthalene from a 50/50 mixture of naphthalene and powdered chalk using carbon dioxide as the extracting solvent is described below. The extraction vessel is first loaded with the solid mixture of naphthalene and powdered chalk. Carbon dioxide is

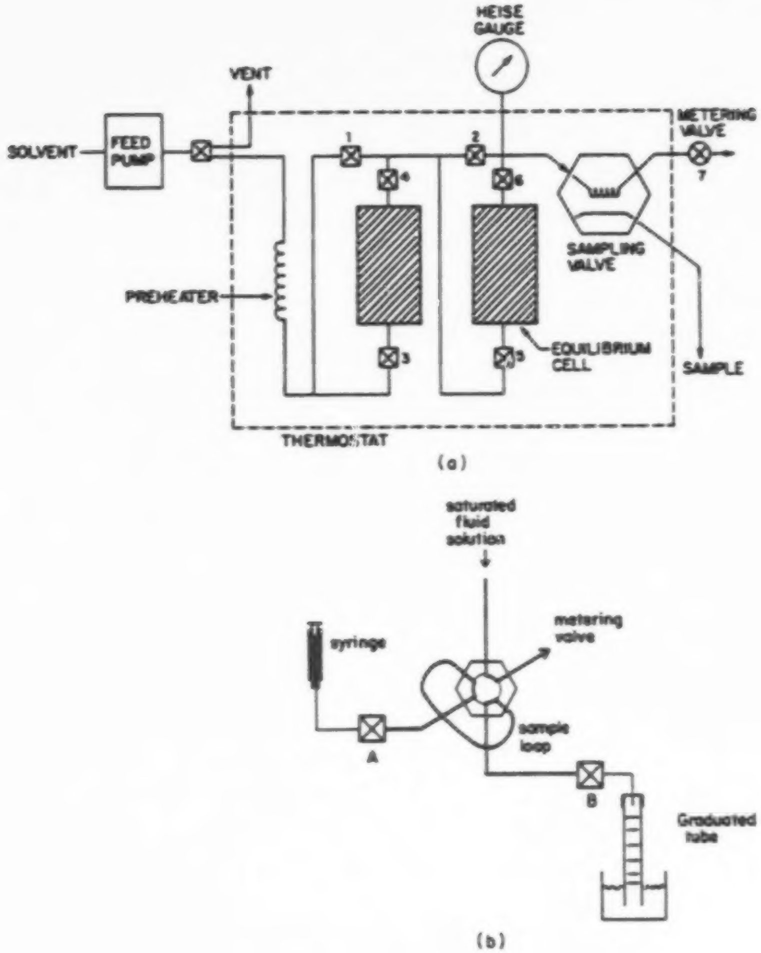

HEISE GAUGE
VENT
SOLVENT
FEED PUMP
METERING VALVE
1
2
4
6
7
SAMPLING VALVE
PREHEATER
EQUILIBRIUM CELL
3
5
SAMPLE
THERMOSTAT
(a)
saturated fluid solution
metering valve
syringe
sample loop
A
B
Graduated tube
(b)

Figure 8. (a) Sampling technique used to obtain solubility information; (b) the setup for removing the sample is depicted (taken from Reference 60).

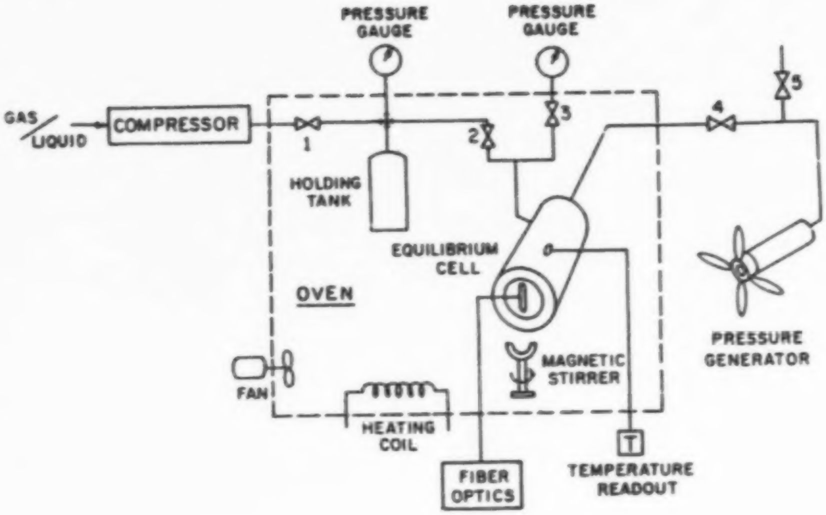
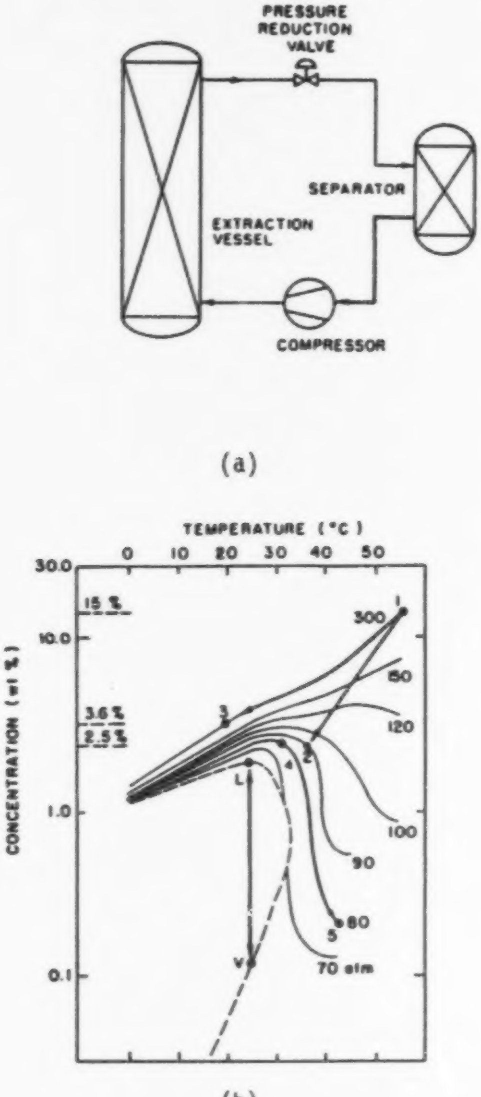

PRESSURE GAUGE
PRESSURE GAUGE
GAS/LIQUID
COMPRESSOR
1
2
3
4
5
HOLDING TANK
EQUILIBRIUM CELL
OVEN
FAN
HEATING COIL
MAGNETIC STIRRER
PRESSURE GENERATOR
FIBER OPTICS
T
TEMPERATURE READOUT

Figure 9. Schematic diagram of a view cell apparatus used to obtain solubilities in an SCF (taken from Reference 61).



(a)

(b)

Figure 10. (a) Schematic diagram of an SFE process; (b) Solubility data for naphthalene in carbon dioxide. Figure taken from Reference 1.

compressed and heated to the desired operating conditions (e.g., 300 atm and 55°C). The pressure reduction valve is activated and the flow of carbon dioxide starts. Naphthalene dissolves in carbon dioxide to a concentration level of 15 wt-percent as is shown by point 1 in Figure 10(b). The carbon dioxide is then expanded to a pressure of 90 atm through the pressure-reduction valve. On lowering the pressure, naphthalene precipitates (see point 2 in Figure 10(b)). If we assume an isenthalpic expansion of the carbon dioxide, a 19°C drop in temperature occurs. Under these conditions (i.e., 90 atm and 36°C), the equilibrium solubility of naphthalene in carbon dioxide is only 2.5 wt-percent. The precipitated naphthalene is collected in a separator and the carbon dioxide stream is recompressed to the initial extraction conditions of 55°C and 300 atm and recycled to the extractor. Thus, changing the pressure of this system (under isenthalpic conditions) has a dramatic effect on the solubility behavior.

Naphthalene can also be extracted isobarically from chalk powder. In this approach, the pressure is kept constant at 300 atm, and the temperature is lowered to 20°C, as shown by point 3 in Figure 10(b). As the carbon dioxide stream is cooled, the concentration of naphthalene decreases from 15 wt-percent to 3.6 wt-percent. The carbon dioxide leaving the separator can then be heated back to 55°C and recycled to the extractor. In this method, the stream leaving the extractor flows through a heat exchanger instead of a pressure-reduction valve, and a blower is incorporated instead of a compressor.

Points 4 and 5 in Figure 10(b) show that a change of 8°C in temperature (from 32 to 40°C) at 80 atm reduces the solubility of naphthalene in carbon dioxide by an order of magnitude. The process can be operated isobarically in this temperature range advantageously.

The dissolving capacity of near-critical liquid carbon dioxide can be utilized as a fourth alternative for carrying out the naphthalene extraction. This method can be understood by the line LV in Figure 10(b). Liquid carbon dioxide near the critical temperature is used to dissolve the naphthalene from the mixture, and the solution leaving the extractor is heated to vaporize the carbon dioxide and recover the naphthalene. The carbon dioxide is then condensed and recycled to the extractor.

The principles of these four modes of operating the SFE of solid substances were discussed from a theoretical point of view. In practice, however, the extraction efficiency is a function of many variables, and a suitable extraction method must be determined based on a number of factors that may be important for a particular application.

SECTION 3

APPARATUS

The SFE technique is now used in a number of chemical processing applications. Recently it has attracted attention for its applicability to analytical purposes, and several new developments have been reported. The SFE technique has also been combined with chromatographic methods such as gas chromatography, SFC, and high-pressure liquid chromatography (HPLC). This section will present the SFE systems that have been reported in the literature.

3.1 OFF-LINE SFE

Various home-made SFE systems and system parts have been described in the technical literature, and some systems are available commercially.

Figure 11 shows a schematic diagram of the apparatus designed by Wright et al. (21). The apparatus consists of three main components: a high-pressure pump, a heated extraction cell, and a depressurization and sample collection system. A modified Rabbit HPX solvent delivery system equipped with a 10-mL/min pump was used to deliver the fluid. The pump head, check valves, and the line leading to the pump were cooled to -15°C by an ethylene glycol-water mixture through copper blocks that were machined to fit the pump-head geometry.

The pressurized fluid was transferred through 1/16-in stainless-steel tubing to the stainless-steel, high-pressure extraction vessel shown in Figure 12 . The extraction vessel could be easily used above 400 bar and 200°C. The extraction vessel was kept inside a gas chromatographic oven.

The transfer line from the pump was long enough to reach the bottom of the extraction chamber (about 5 mL volume) where the sample was placed in a 5.4-cm x 1.3-cm OD borosilicate glass test tube. This allowed the SCF to flow from the bottom to the top of the extraction chamber. The SCF carrying the organics was collected by freezing in a sealed round-bottom flask cooled in liquid nitrogen. This method ensured that no analyte losses to the atmosphere occurred during collection.

Hawthorne and Miller (26) used an extraction cell which was constructed of 316 stainless-steel fittings shown in Figure 13. This cell had an internal volume of 0.1 mL.

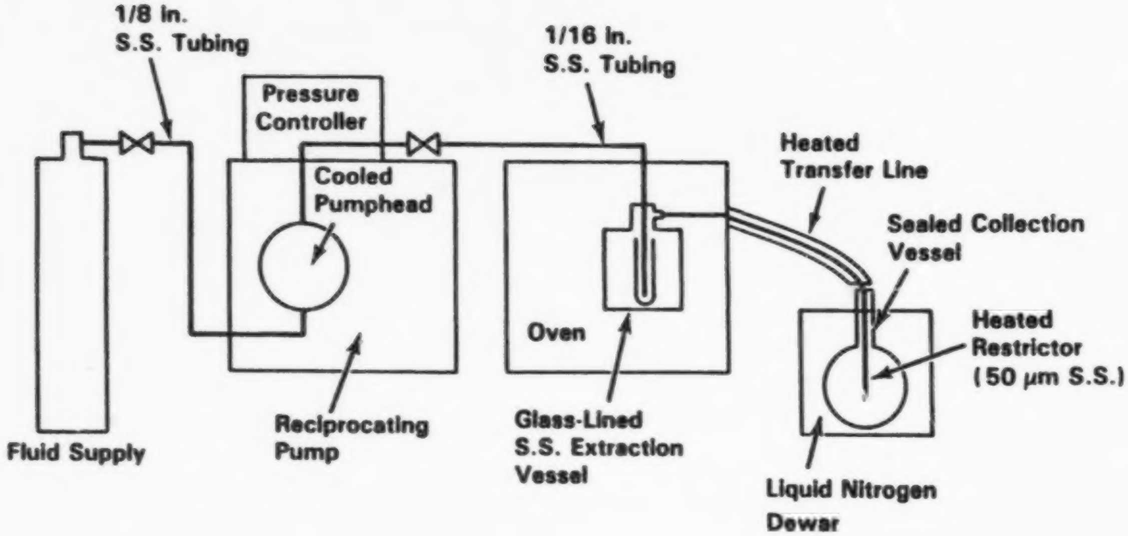

1/8 in.
S.S. Tubing
Pressure
Controller
1/16 in.
S.S. Tubing
Heated
Transfer Line
Cooled
Pumphead
Sealed Collection
Vessel
Oven
Heated
Restrictor
(50 μm S.S.)
Fluid Supply
Reciprocating
Pump
Glass-Lined
S.S. Extraction
Vessel
Liquid Nitrogen
Dewar

Figure 11. Schematic diagram of the off-line SFE apparatus (taken from Reference 21).

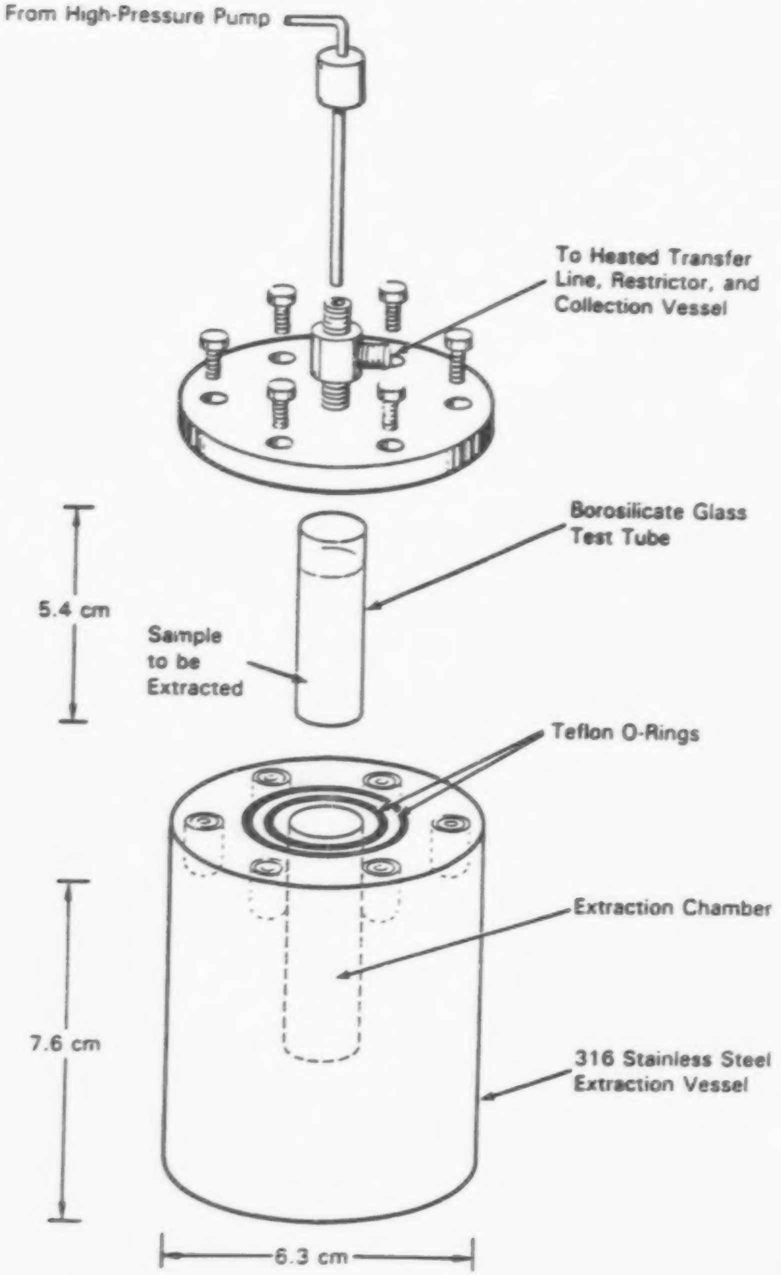

From High-Pressure Pump
To Heated Transfer Line, Restrictor, and Collection Vessel
Borosilicate Glass Test Tube
5.4 cm
Sample to be Extracted
Teflon O-Rings
Extraction Chamber
7.6 cm
316 Stainless Steel Extraction Vessel
6.3 cm

Figure 12. Design of SFE vessel (taken from Reference 21).

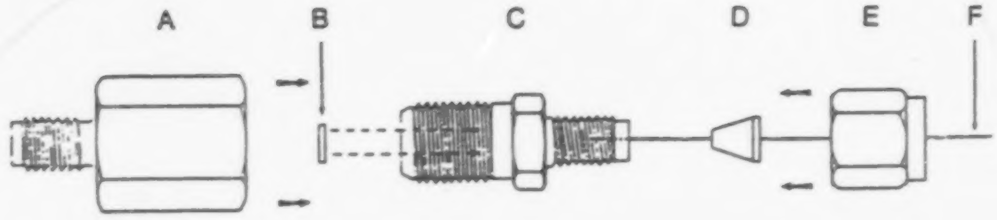


Figure 13. SFE cell for coupled SFE-GC analysis. The components of the cell are (A) 1/16-in female NPT x 1/16-in tubing union, (B) 0.5-µm x 1/8-in OD stainless-steel frit, (C) 1/16-in male NPT x 1/16-in tubing union, (D) 15 percent graphite - 85 percent polyimide ferrule, (E) 1/16-in nut, and (F) fused-silica capillary restrictor. All fittings were stainless-steel "Parker" brand (taken from Reference 26).

Schantz and Chesler (19) used a 25-cm x 6.35-mm OD stainless-steel column packed with approximately 6 g of sediment. The inlet of the column was connected to the carbon dioxide inlet of the supercritical fluid chromatograph, and the outlet was connected to a 66-cm section of 60-µm ID fused-silica capillary. The capillary served to reduce the pressure of the carbon dioxide to ambient pressure.

Sugiyama and Saito (84) built two types of micro-SFE systems using a JASCO Model BIP-1 pump with cooling jacket. The extraction cell was made of 35-mm x 4.6-mm ID stainless-steel tubing. A 5-m x 0.5-mm ID stainless-steel tube connected the pump and the extraction cell. This tube was coiled and kept in an HPLC column oven to serve as a heat exchanger. In one of the systems built by Sugiyama and Saito (84), the extraction was monitored with an UV detector and the flow of carbon dioxide was monitored with a mass-flow meter installed behind the back-pressure regulator. In their other system, a 25-cm x 0.25-mm ID stainless-steel tube was used as a restrictor instead of the back-pressure regulator. The restrictor was crimped with a pair of pliers to increase the flow resistance.

Eisenbach (62) described a scheme for SFE involving the use of extraction and separation vessels with an intermediate heat exchanger and a fractionation column. A hot finger heats the supercritical carbon dioxide and reduces its density. This results in a decrease in solubility of all solutes in the supercritical fluid, but not to the same extent. The more soluble components are extracted and pass into the separation vessel to be recovered by precipitation at reduced pressure, whereas the less soluble components return to the separation vessel. The recovered fractions then become the starting material for the second fractionation step and the process is repeated. This method is useful for the concentration of fatty acids from fish oil.

Recently we have contacted six manufacturers: Computer Chemical Systems of Avondale, Pennsylvania; Lee Scientific of Salt Lake City, Utah; Hewlett Packard Corporation of Avondale, Pennsylvania; Suprex Corporation of Pittsburgh, Pennsylvania; ISCO of Lincoln, Nebraska; and JASCO of Tokyo, Japan, tha have developed commercial units for SFE. Below is a brief discussion of the commercially available equipment.

Suprex offers three systems: the SFE/10, the SFE/50, and the MPS/225. The SFE/10 microextraction system is designed for use with SFC. It has two sets of switching valves, a 1-mL extraction cell, an extraction heater, and the appropriate hardware/software to connect into the pumping and the electronics of the Suprex model SFC/100A, SFC/150A, or SFC/200 instrument. The Suprex SFE/50 system is a free-standing unit and consists of:

- One 250-mL stepper-motor-driven syringe pump
- Instrument electronic control system including the mobile phase delivery controllers for pressure programming
- Extractor oven (maximum operating temperature is 200°C)
- 4-Port selector valve
- Startup kit (fittings, tubing, extraction cells (Figure 14), etc.)
- Solvent modifier valve to add modifiers to the pump
- Carbon dioxide density programming system.

Figure 15 shows a schematic diagram of the Suprex unit. The extractor cell consists of a machined stainless-steel vessel which is connected at either end to 1/16-in OD stainless-steel tubing. The sample is retained between two Kel-F frits of 2-μm porosity. The volume of the extractor cells varies from 0.5 mL to 50 mL. The SFE unit is operated as follows: the sample is charged to the extractor cell, the switching valve is in position 1, and valve I is closed. The extractor cell is filled with

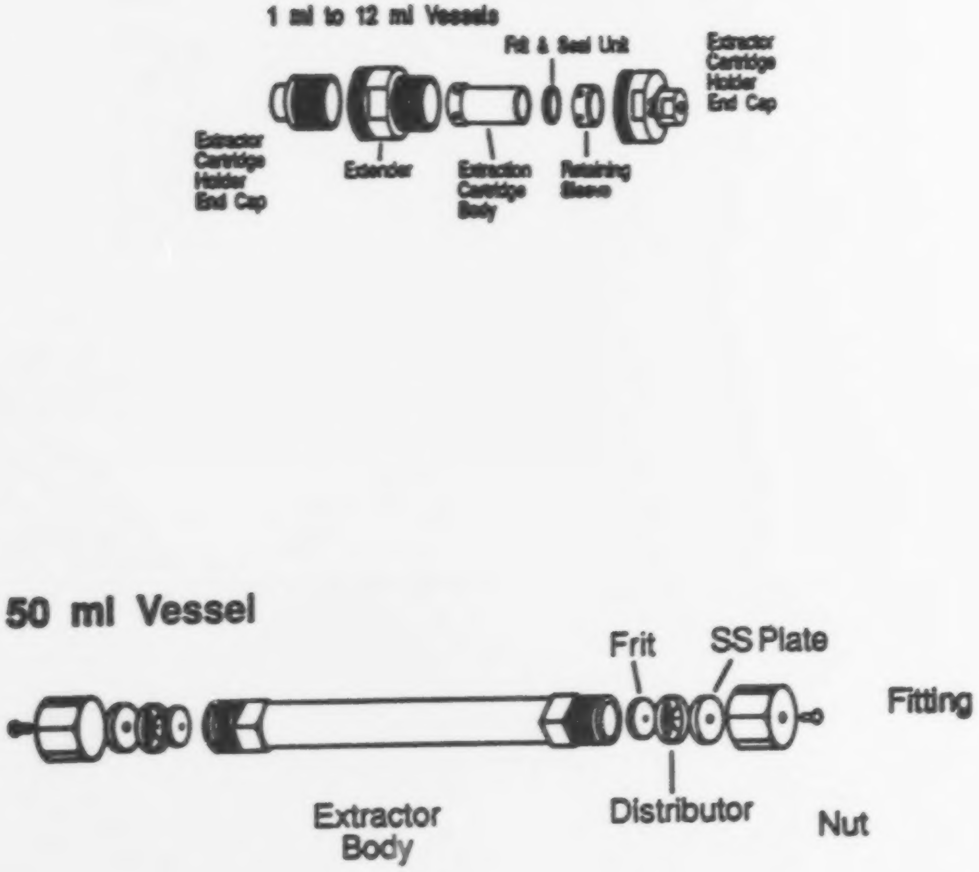

1 ml to 12 ml Vessels
Frit & Seal Unit
Extractor Cartridge Holder End Cap
Extractor Cartridge Holder End Cap
Extender
Extraction Cartridge Body
Retaining Sleeve
50 ml Vessel
Frit
SS Plate
Fitting
Extractor Body
Distributor
Nut

Figure 14. Extraction vessels available from Suprex Corporation.

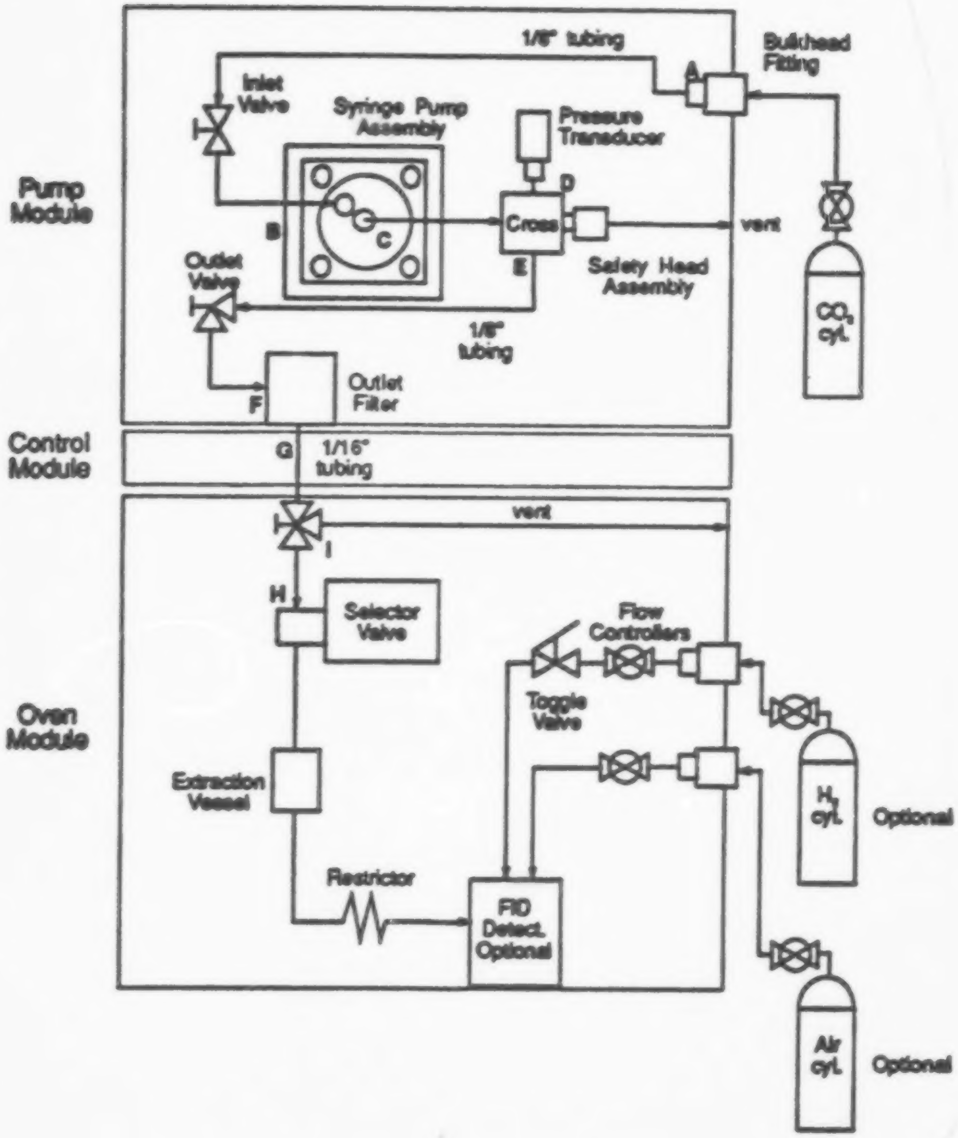

1/8" tubing
Bulkhead Fitting
A
Inlet Valve
Syringe Pump Assembly
Pressure Transducer
D
Pump Module
B
Cross
C
vent
Outlet Valve
E
Safety Head Assembly
1/8" tubing
CO2 cyl.
Outlet Filter
F
Control Module
G
1/16" tubing
vent
I
H
Selector Valve
Flow Controllers
Toggle Valve
Oven Module
Extraction Vessel
H2 cyl.
Optional
Restrictor
FID Detect. Optional
Air cyl.
Optional

Figure 15. Schematic diagram of the Suprex SFE/50 extraction system.

the SCF from the syringe pump and is allowed to equilibrate at the desired temperature and pressure. After equilibration, the system switches automatically to the "run" mode, and the SCF containing the organic compounds removed from the matrix passes through the restrictor to the collection vessel (static extraction).

The Suprex SE/50 system is equipped with a four-position selector valve that allows static extraction for a defined period of time and collection of three fractions per sample in the dynamic mode (Figure 16) or collection of four fractions per sample in the dynamic mode but without static extraction.

The Suprex MPS/225 system was introduced at the 1990 Pittsburgh Conference in New York City. It is a state-of-the-art, coupled SFE-SFC system with cryogenic trapping. The system can be used either as a stand-alone SFE system or a stand-alone SFC system (Figure 17). The syringe pump is a 250-mL pump, driven by a stepper motor, and has an electronically-actuated, microprocessor-controlled valve which refills the pump automatically.

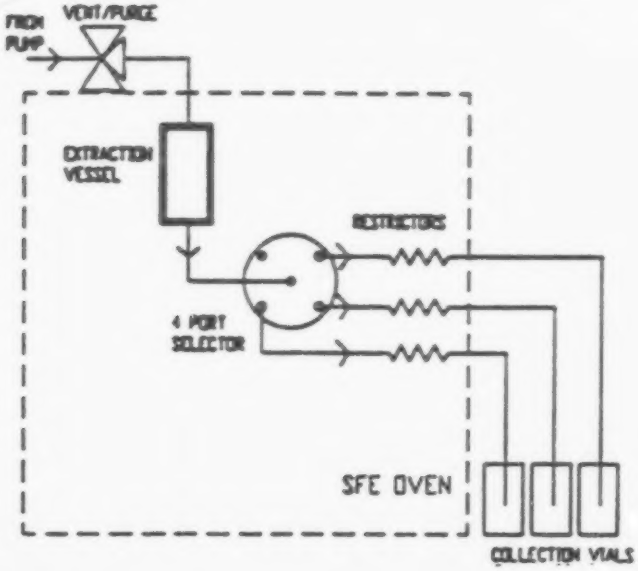
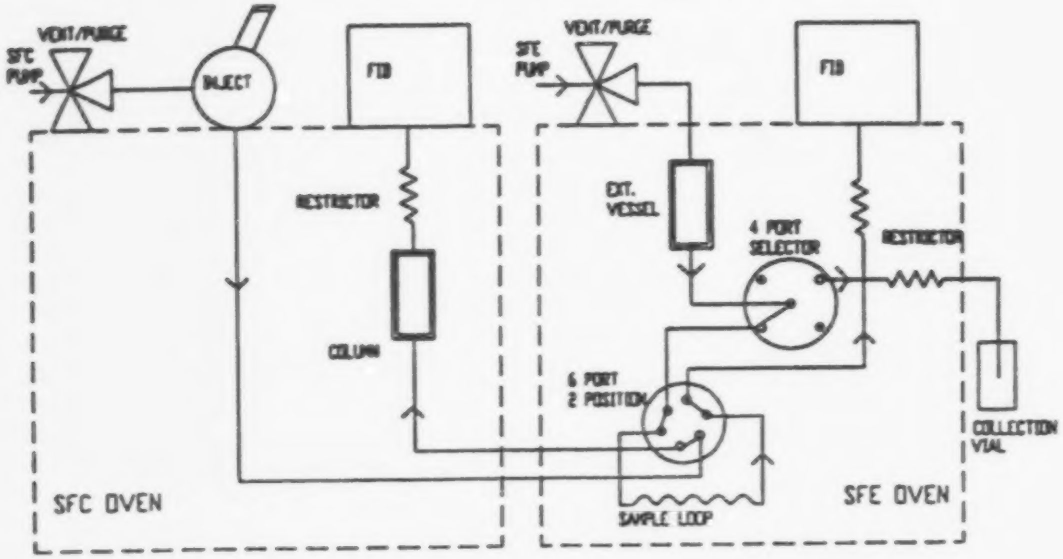
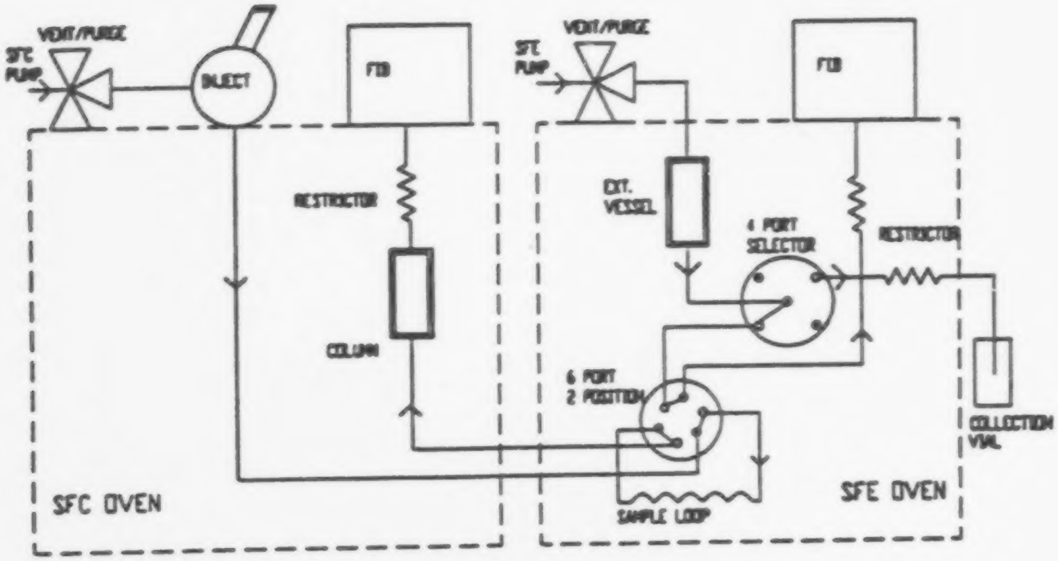


Figure 16. Schematic diagram of four-port selector valve with restrictors and collection vials.


VENT/PURGE
SFC PUMP
INJECT
FID
RESTRICTOR
COLUMN
SFC OVEN
VENT/PURGE
SFE PUMP
FID
EXT. VESSEL
4 PORT SELECTOR
RESTRICTOR
6 PORT 2 POSITION
COLLECTION VIAL
SAMPLE LOOP
SFE OVEN

SFE-SFC in Load Position


VENT/PURGE
SFC PUMP
INJECT
FID
RESTRICTOR
COLUMN
SFC OVEN
VENT/PURGE
SFE PUMP
FID
EXT. VESSEL
4 PORT SELECTOR
RESTRICTOR
6 PORT 2 POSITION
COLLECTION VIAL
SAMPLE LOOP
SFE OVEN

SFE-SFC Inject Position

Figure 17. Schematic diagram of the MPS/225 SFE system from Suprex.

Computer Chemical Systems, Inc. (CCS), offers a Model 3000 Series SFE/accumulator for either off-line extractions or direct coupling to a SFC. The Model 3100 extractor consists of the extractor/accumulator module, a controller with keyboard and display, and a pump. The pump is capable of operation to 10,000 psi; it is an air-operated pump, requiring 70 psi of compressed air to reach 10,000 psi operating pressure. The system is normally operated as a dynamic extractor. The extracted components are typically carried onto a cryogenic accumulator, although the collection into an organic solvent is also feasible. The accumulator column ensures that the lower-molecular-weight compounds are not lost in the transfer from the SFE to the SFC. For SFE-SFC operation, the SFC column is connected and the cryofocused extract is desorbed from the accumulator directly onto the SFC column.

CCS introduced at the 1990 Pittsburgh Conference in New York City a multivessel extraction system that allows extraction of up to six samples simultaneously. No diagrams of the instrument were available from CCS at the time this report was written.

Lee Scientific, Inc., offers an extraction system that is not a stand-alone unit, however, it can be used with an SFC. The extraction system consists of a switching valve, column interface, extraction cell, heater control, and associated hardware, and it can be mounted on the Lee Scientific Model 501 and Series 600 ovens. The cell is made of stainless-steel, and is available in 300-µL and 850-µL volume sizes. The temperature of the cell can be varied from 40°C to 150°C.

ISCO, Inc., has a two-extraction-vessel system (Model SFX 2-10) with dual-extraction chambers with independent valving. Quick-load cartridges hold sample volumes of up to 10 mL; use of wrenches for tightening is not required (Figure 18). The Model 260D syringe pump is a pulse-free pump of 260-mL capacity, can handle flowrates of up to 100 mL/min, and has a pressure rating of 7,500 psi (525 atm). The controller module allows simultaneous operation of up to three pumps, thus allowing to run composition gradients, to introduce modifiers into the fluid stream, and to continuously deliver fluid with alternating refill.

The systems described above use a fused-silica restrictor as a back-pressure regulator. The two systems that are described below from JASCO Inc. and Hewlett Packard use a back-pressure regulator device to maintain the pressure inside the extraction vessel at the desire setting. The JASCO Model Super-200S (Figure 19) has four components: the fluid delivery module, the extraction and chromatography module, the UV detector, and the fractionation module. The fluid delivery system has two pumps, one for carbon dioxide delivery and the other for modifier delivery. The back-pressure regulator allows pressure control without changing the flowrate of carbon dioxide. Furthermore, the low internal dead-volume of the back-pressure regulator (<10 µL) allows a sharp cutoff between fractions. In addition, the JASCO system is equipped with a photodiode-array UV detector that allows real-time UV monitoring of column effluent.

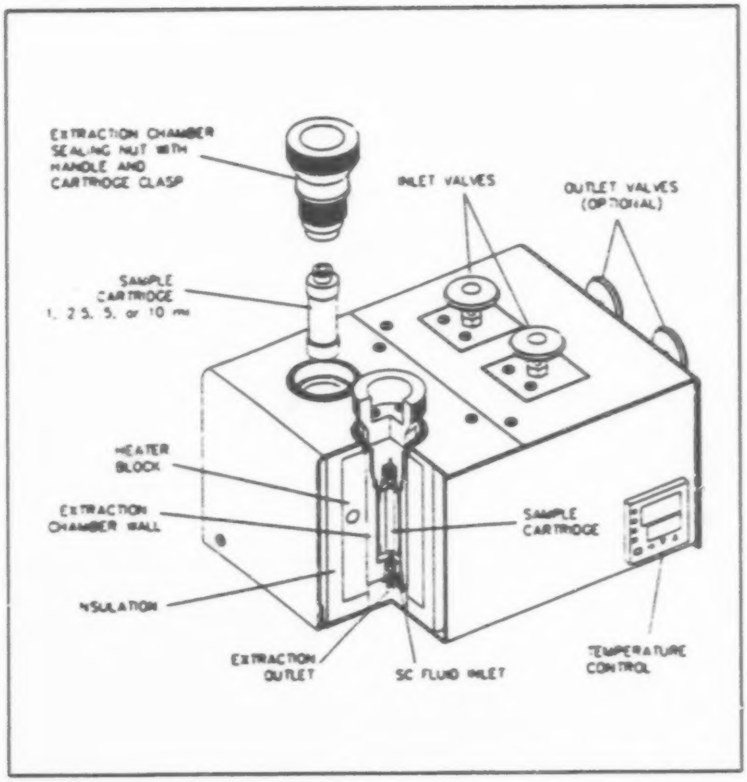

EXTRACTION CHAMBER SEALING NUT WITH HANDLE AND CARTRIDGE CLASP
INLET VALVES
OUTLET VALVES (OPTIONAL)
SAMPLE CARTRIDGE 1, 2.5, 5, or 10 ml
HEATER BLOCK
EXTRACTION CHAMBER WALL
SAMPLE CARTRIDGE
INSULATION
EXTRACTION OUTLET
SC FLUID INLET
TEMPERATURE CONTROL

Figure 18. The ISCO SFX 2-10 extraction module.

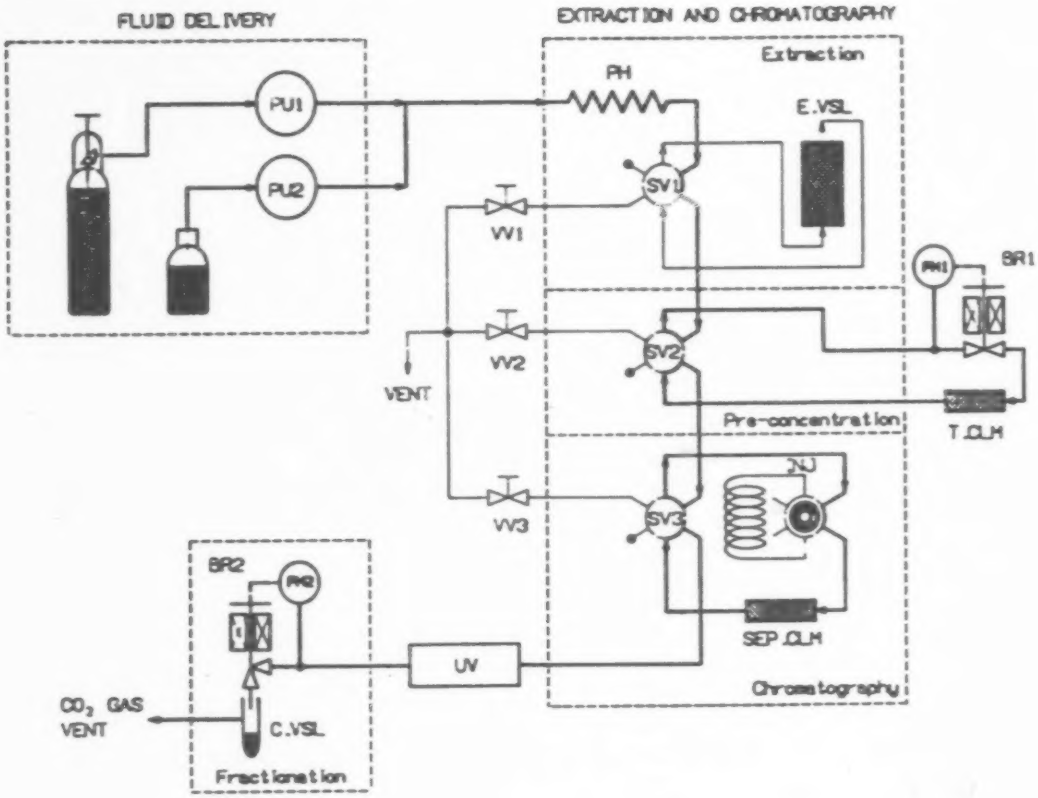

FLUID DELIVERY
EXTRACTION AND CHROMATOGRAPHY
Extraction
PH
E.VSL
PU1
PU2
SV1
VV1
PM1
BR1
VV2
SV2
VENT
Pre-concentration
T.CLM
INJ
VV3
SV3
SEP.CLM
BR2
PM2
UV
Chromatography
CO₂ GAS VENT
C.VSL
Fractionation

Figure 19. Schematic diagram of Jasco Model SUPER-200S.

The Hewlett Packard Model 7680A also features a back-pressure regulator and an accumulator column for the collection of the organic compounds from the SCF as the fluid depressurizes. An interesting feature on the Hewlett Packard extractor is the display screen (Figure 20), which shows all the set points for the extraction and the flow path for both extraction fluids and rinse solvents. The organic compounds are collected on an accumulator column (C_{18}-bonded silica or stainless-steel beads); to recover the compounds, the accumulator column is rinsed with an organic solvent. Two different solvents can be used and up to 21 fractions can be collected.

3.2 ULTRASONIC SFE

Variations in density and pressure, which have the potential of improving solute diffusion and enhancing overall extraction, can be created by the application of ultrasound during SFE. These ultrasound waves are expected to induce convection of solutes from the inner pores of a material. They also create localized heating that could enhance the desorption rate of solutes from a matrix. Sonication may also improve extractions by changing the internal structure of a porous material.

The ultrasonic SFE apparatus described by Wright et al. (64) is shown in Figure 21. It consists of a 25-mL high-pressure stainless-steel cell which is equipped with two 0.75-in diameter windows for observation during extraction and a high-power ultrasonic horn. The useable cell volume underneath the horn was approximately 12 mL. The ultrasonic transducer was connected to the extraction vessel through an O-ring seal. The extraction vessel was placed in a water-bath. A magnetically coupled gear pump was used to recirculate the fluid inside the vessel through a coil of 1/8-in OD stainless-steel tubing. An UV absorbance detector equipped with a high-pressure flow cell was used to monitor the concentration of extracted analytes.

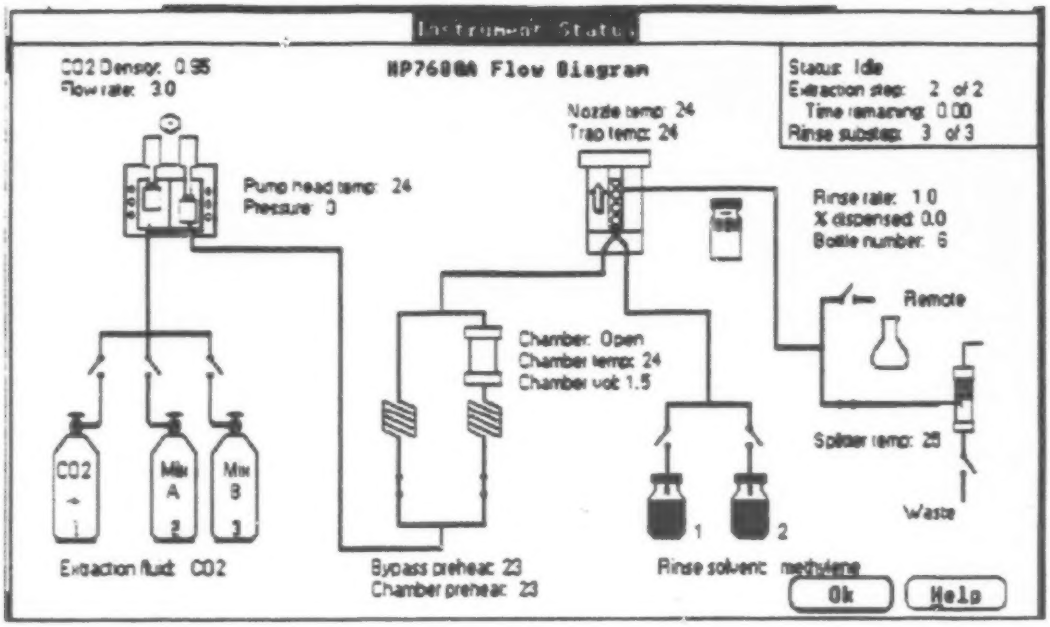
3.3 ON-LINE SFE

Various types of on-line designs have been reported, including continuous monitoring of the SFE effluent by gas chromatography (20), mass spectrometry (45,84), combined SFE-HPLC (66), and combined SFE-SFC (40,67).

We briefly describe below the on-line SFE gas chromatography system used by Wright et al. (20). A schematic diagram of the apparatus is shown in Figure 22. It consists of a high-pressure pump, an extraction cell, a switching valve and interface region, a gas chromatograph with a flame ionization detector, and a minicomputer and its associated interface circuitry.

A modified Varian 8500 syringe pump was used to supply the high-pressure carbon dioxide to the extraction cell. The microextraction cell shown in Figure 23 was constructed from Swagelok stainless-steel zero volume 1/4-in to 1/16-in column-end fittings containing two 1/4-in OD

Reproduced from
best available copy.


Instrument Status
HP7680A Flow Diagram
CO2
Mix A
Mix B
1
2
3
Remote
Waste
1
2
Ok
Help

CO2 Density: 0.95
Flow rate: 3.0
Pump head temp: 24
Pressure: 0
Nozzle temp: 24
Trap temp: 24
Status: Idle
Extraction step: 2 of 2
Time remaining: 0.00
Rinse substep: 3 of 3
Rinse rate: 1.0
% dispensed: 0.0
Bottle number: 6
Chamber: Open
Chamber temp: 24
Chamber vol: 1.5
Splitter temp: 25
Extraction fluid: CO2
Bypass preheat: 23
Chamber preheat: 23
Rinse solvent: methylene

Figure 20. Display screen for the Hewlett Packard Model 7680A extractor.

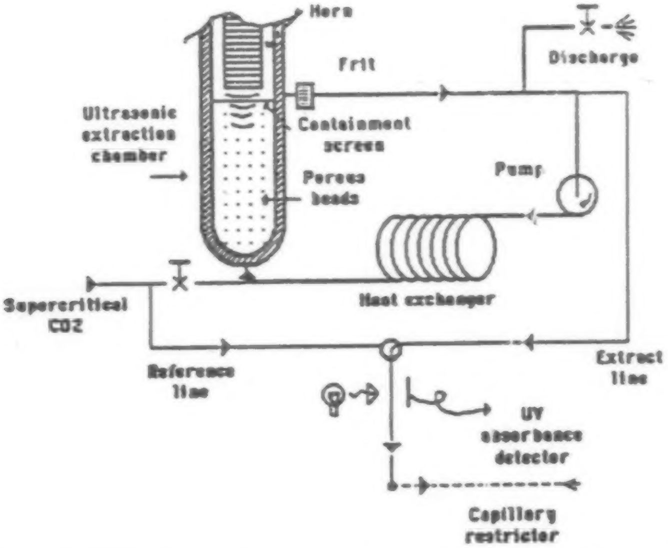

Horn
Frit
Discharge
Ultrasonic extraction chamber
Containment screen
Porous beads
Pump
Heat exchanger
Supercritical CO2
Reference line
Extract line
UV absorbance detector
Capillary restrictor

Figure 21. Schematic diagram of the ultrasonic SFE apparatus (taken from Reference 64).

178

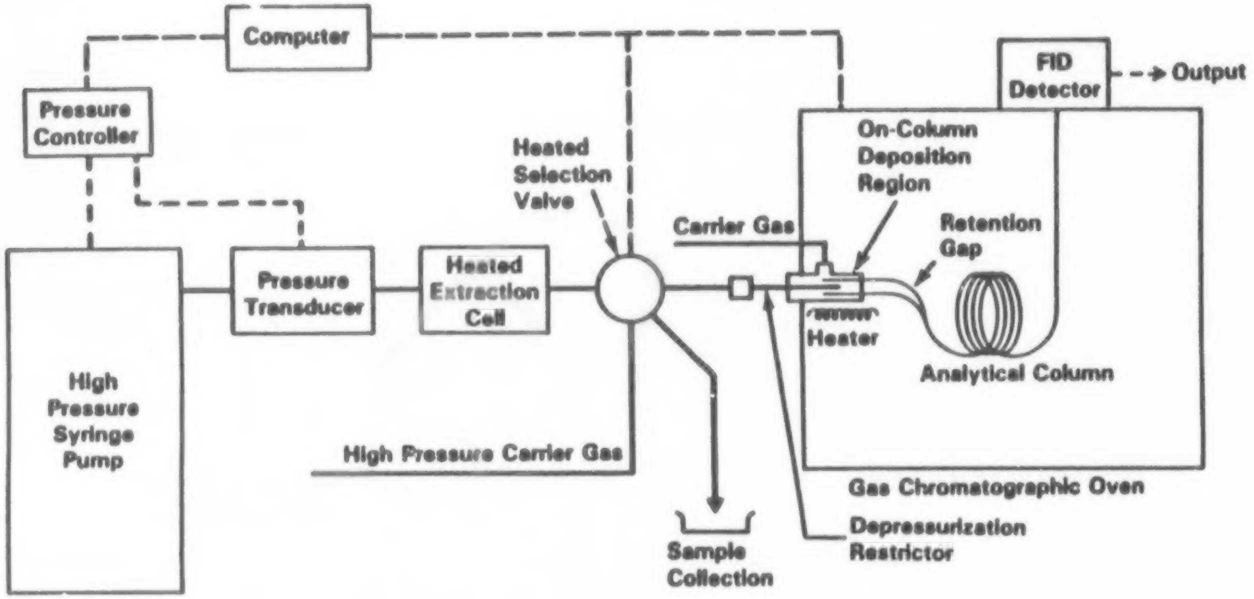

Computer
Pressure Controller
FID Detector
Output
On-Column Deposition Region
Heated Selection Valve
Carrier Gas
Retention Gap
Pressure Transducer
Heated Extraction Cell
Heater
Analytical Column
High Pressure Syringe Pump
High Pressure Carrier Gas
Gas Chromatographic Oven
Depressurization Restrictor
Sample Collection

Figure 22. Schematic diagram of the on-line SFE interfaced to a gas chromatograph (taken from Reference 20).

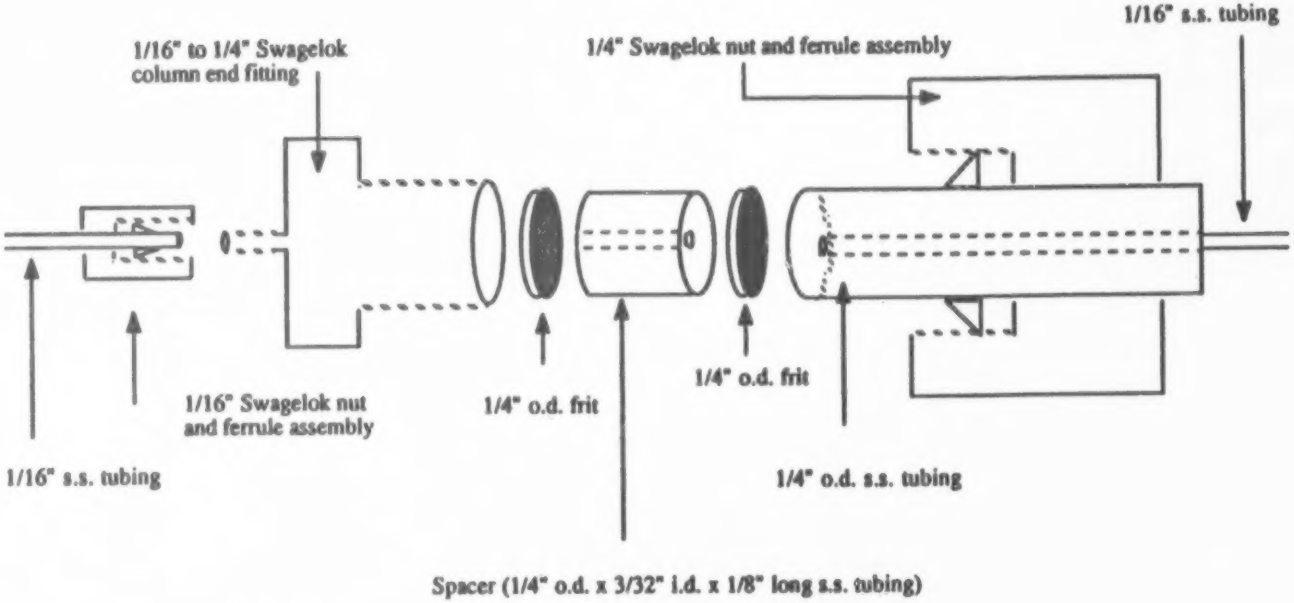

1/16" to 1/4" Swagelok column end fitting
1/4" Swagelok nut and ferrule assembly
1/16" s.s. tubing
1/16" Swagelok nut and ferrule assembly
1/4" o.d. frit
1/4" o.d. frit
1/4" o.d. s.s. tubing
1/16" s.s. tubing
Spacer (1/4" o.d. x 3/32" i.d. x 1/8" long s.s. tubing)

Figure 23. Design of the microextraction cell (taken from Reference 20).

sintered stainless-steel frits with 2-μm pore size, separated by a 1/8-in stainless-steel insert. A Rheodyne 7010 six-post switching valve had been used to direct the extraction cell effluent to either an exterior collection reservoir or to the gas chromatographic column. Fused-silica tubing (5 μm ID x 2-4 cm length) was used as depressurization restrictor and to maintain supercritical pressures up to the point of on-column deposition or sample collection. When used for on-column deposition, the restrictor was mounted through a 1/16-in tee to allow the carrier gas to enter coaxially along the restrictor. A Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector was used for chromatographic analysis.

The instrumentation used for SFE-mass spectrometry is shown in Figure 24. A Varian 8500 syringe pump was used to deliver the SCF to the extraction vessel. The pump was modified to allow pressure programming capability. The effluent from the extraction cell was injected into the ion source of the mass spectrometer through 50-μm ID deactivated fused-silica tubing. A 2- to 3-cm piece of 5-μm ID fused-silica tubing served as restrictor to allow depressurization of the SFE effluent prior to entering the ion source of the mass spectrometer. The restrictor tip was heated at 350°C to prevent freezing of the fluid during depressurization.

Hawthorne et al. (48,49) transferred the extract from the SFE cell directly into the gas chromatographic column by inserting the outlet restrictor into the gas chromatographic column through the on-column injection port. Both GC/FID and GC/MS were used to quantitate polycyclic aromatic hydrocarbons and PCBs in environmental samples. Various restrictors of internal diameters ranging from 15 μm to 40 μm were tested. The gas chromatographic oven was maintained at -50°C to 25°C throughout the 10-min extraction. Supercritical carbon dioxide at 300 atm and 45°C was employed. In the case of SFE-GC/FID, a 30-m x 0.32-mm ID DB-5 fused-silica column (1.0-μm film thickness) gave successful results. Attempts to use the same gas chromatographic conditions for the GC/MS analysis were unsuccessful because of the high pressure in the mass spectrometer ion source. A 60-m narrow-bore DB-5 fused-silica capillary column (0.25-mm ID x 0.25-μm film thickness) allowed acceptable source pressure during the extraction step. After the extraction was completed, the column was flushed with carrier gas for 3 min to remove the carbon dioxide.

Hawthorne and Miller (48) also coupled the SFE technique to GC/ECD. Since the nitrous oxide they used as fluid gives a relatively high ECD response, the column had to be flushed with carrier gas for 2 to 3 min after extraction. After the flushing step, the column was rapidly heated to 200°C followed by temperature programming at 8°C/min to 320°C.

Coupling of SFE to SFC was reported by McNally and Wheeler (40). The apparatus used was a Hewlett-Packard Model 1082 liquid chromatograph modified to accommodate SCFs. A circulating ethylene glycol bath cools the pump heads of the two diaphragm pumps. The normal UV cell was replaced with a high-pressure cell, and a back-pressure regulator was installed

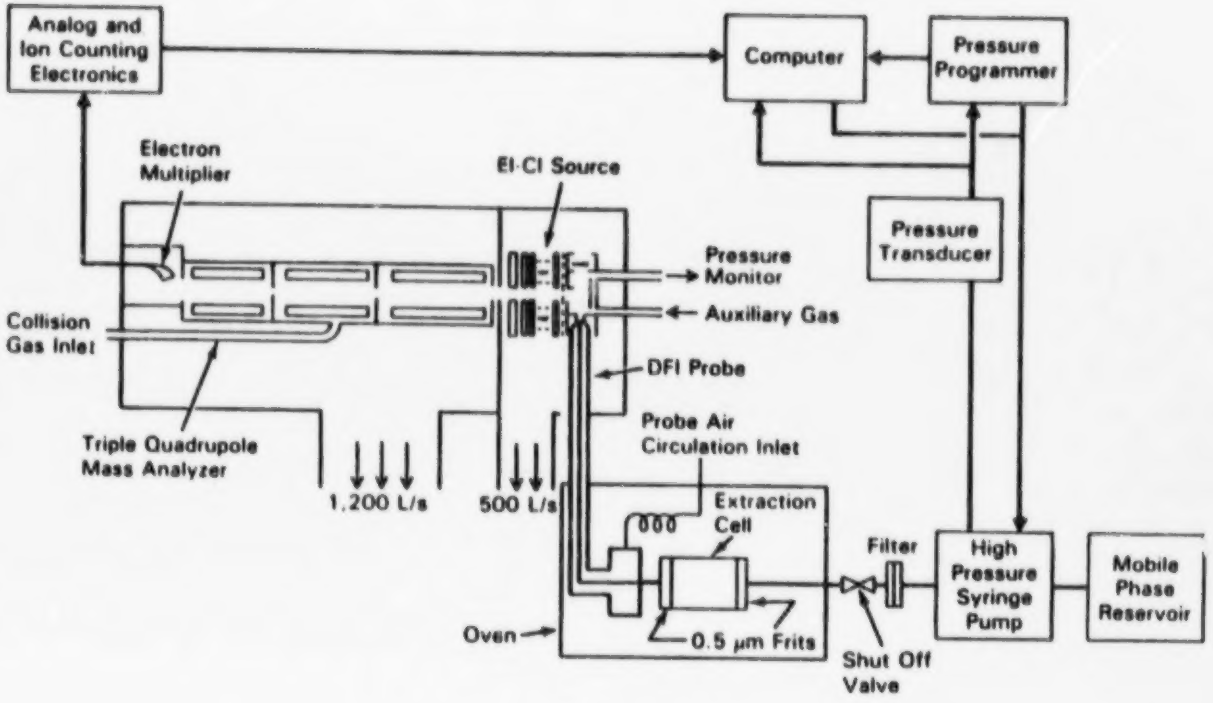

Analog and Ion Counting Electronics
Computer
Pressure Programmer
Pressure Transducer
Electron Multiplier
EI·CI Source
Pressure Monitor
Auxiliary Gas
Collision Gas Inlet
DFI Probe
Triple Quadrupole Mass Analyzer
Probe Air Circulation Inlet
1,200 L/s
500 L/s
Extraction Cell
Filter
High Pressure Syringe Pump
Mobile Phase Reservoir
Oven
0.5 μm Frits
Shut Off Valve

Figure 24. Schematic diagram of the direct SFE-mass spectrometry instrumentation (taken from Reference 20).

between the detector and the waste stream to allow the mobile phase pressure to be varied within supercritical conditions.

The extraction cell consisted of an empty 25-cm x 4.6-mm ID liquid chromatography column. Other sizes were also used; all columns were pressure-rated to withstand 4,200 psi at temperatures up to 100°C.

The switching valve, shown in Figure 25, consists of a Rheodyne Model 7040 dual switching valve coupled to a Rheodyne Model 5704 tandem actuator with pneumatic control. The valve can be operated in two positions. In the position A, the mobile phase enters the valve, travels through the extraction cell and the sample loop, reaches the UV detector, then the back-pressure regulator and the collector. In the second position, the flow bypasses the extraction cell and flushes the portion of sample left in the sample loop directly onto the analytical column.

The collection device employed by McNally and Wheeler (40) is shown in Figure 26. The 1/4-in stainless-steel tubing that exits the back-pressure regulator is rerouted to the tubing that connects to the solvent reservoir flask. The SCF carrying the organics extracted from the sample passes through the solvent reservoir frit and is collected in the glass reservoir. The pressure of the fluid entering the solvent reservoir is below 1,000 psi.

Other reports published recently on coupling SFE to GC and SFC include work done by Hawthorne et al. (127), Levy et al. (131), Xie et al. (133), and Liebman et al. (134). Hawthorne et al. (127) reported that SFE can be coupled directly with capillary gas chromatography using a commercially available septumless injector. Since the SFE effluent is depressurized directly in the injection port of a gas chromatograph, problems experienced with plugging of the restrictor are eliminated. Samples analyzed by this technique included: a fuel-contaminated sediment, the NIST Standard Reference Material 1941 (marine sediment), and a few polyurethane foam plugs. Samples as large as 15 g were analyzed in 1 hr, including extraction, analyte concentration, and gas chromatographic analysis (127).

Multidimensional SFC-SFE was reported by Levy et al. (131); it involves a multistep heatcutting of fractions from an SFC to a capillary gas chromatograph. The effectiveness of this technique was demonstrated on complex samples of heavy hydrocarbons and in polymer fingerprinting.

An SFE-SFC-fraction collection system was reported by Xie et al. (133). In this system, the SFE extract was decompressed through a small-ID linear restrictor and the extracted material deposited in a deactivated capillary solute concentrator within a cryogenic trap. The capillary solute concentrator was connected directly to the SFC column. After some defined period of time, the SFE was discontinued and the SFC was started with a density-programmed mobile phase. Fractions of the effluent were collected in a solvent using a frit restrictor at the column outlet.

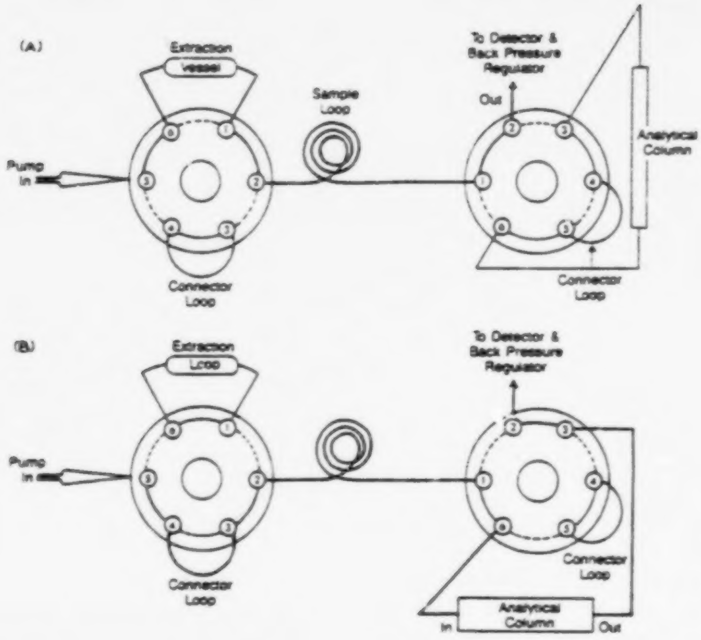

(A)
Extraction
Vessel
Sample
Loop
To Detector &
Back Pressure
Regulator
Out
Pump
In
Analytical
Column
Connector
Loop
Connector
Loop
(B)
Extraction
Loop
To Detector &
Back Pressure
Regulator
Pump
In
Connector
Loop
Connector
Loop
Analytical
Column
In
Out

Figure 25. Flow diagrams of the switching valve (A) in the extraction position, and (B) in the chromatographic analysis positions (taken from Reference 40).

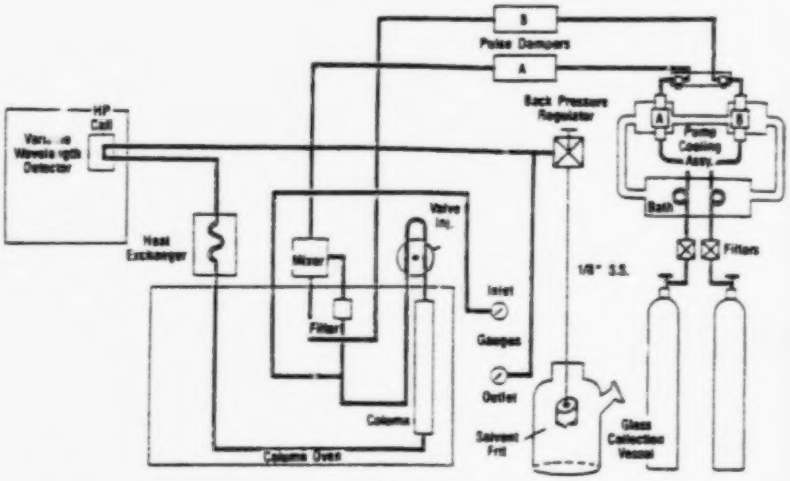

B
Pulse Dampers
A
HP
Cell
Variable
Wavelength
Detector
Back Pressure
Regulator
A
B
Pump
Cooling
Assy.
Bath
Filters
Heat
Exchanger
Mixer
Filter
Valve
Inj.
Inlet
Gauges
Outlet
1/8" S.S.
Column
Column Oven
Solvent
Frit
Glass
Collection
Vessel

Figure 26. Schematic diagram of the HP1082 supercritical fluid chromatograph with solvent reservoir as collection vessel (taken from Reference 40).

To help in sample processing, on-line analysis, and data processing, Liebman et al. (134) reported on an automated SFC/GC system that uses an artificial intelligence network called microEXMAT. This software system provides the chemist with a problem-solving guide for the SFE technique that includes analytical strategy, instrument configuration, methods development, data analysis, and interpretation.

SECTION 4

APPLICATIONS

Numerous applications of SFE have been reported, most of them developed recently. Table 4 shows some of the applications. In this section we will emphasize only those applications relevant to our work.

4.1 MATRIX/SCF/ENTRAINER EFFECTS

Brady et al. (18) have investigated SFE of PCBs, DDT, and toxaphene from contaminated soils using supercritical carbon dioxide at 40°C and 100 atm. They showed that approximately 70 percent of the DDT and 75 percent of the toxaphene can be leached from a topsoil spiked with 1,000 ppm DDT and 400 ppm toxaphene in under 10 min by using supercritical carbon dioxide at a rate of 0.7 g/sec. The extraction of PCB-spiked subsoil resulted in recoveries higher than 90 percent in 1 min under the same conditions and at the same carbon dioxide flowrate. The organic and water contents of the soil were found to be the two primary factors affecting the extraction efficiency.

In the case of DDT, 60 to 70 percent of the amount present in the soil can be extracted in approximately 10 to 20 min. Similar results were obtained for material spiked in the laboratory. The extraction of PCBs was more efficient since 99 percent removal was achieved in 1 min. The authors attributed the higher recovery of PCBs to the fact that Cecil subsoil contains only 0.74 percent organic carbon whereas the contaminated subsoil contained 12.6 percent organic carbon. The higher concentration of the organic carbon in the case of the contaminated subsoil contributed to the slow release of DDT from the top soil and thus to lower recoveries. Furthermore, the mild acidity of the DDT may have contributed to stronger adsorption of DDT onto the soil particles.

Extraction of organic compounds from urban particulate matter and from sediments under supercritical conditions was investigated by Schantz and Chesler (19). Samples of 1 g (urban particulate matter) to 6 g (sediment) were extracted with supercritical carbon dioxide at 40°C and

TABLE 4. EXAMPLES OF APPLICATIONS OF SFE REPORTED IN THE LITERATURE

Compound	Matrix	SCF	Reference
PCBs, DDT, toxaphene	Contaminated soils	Carbon dioxide	18
PAHs, PCBs	Urban particulates, sediments	Carbon dioxide	19
Chrysene, benzanthrone, 1-nitropyrene, dibenzo(a,i)carbazole, coronene, decacyclene	XAD resin PUF, urban dust	Carbon dioxide, isobutane, carbon dioxide with 20 mole percent methanol	21,42,64
γ-BHC, parathion, hexachlorobiphenyl, anthracene	Tenax-GC, polyimide sorbents	Carbon dioxide	24,86
PAHs	Urban dust (SRM-1649)	Carbon dioxide, nitrous oxide, ethane; with and without modifiers (methanol)	25,26
^{14}C-Atrazine, ^{14}C-prometryn, ^{14}C-deltamethrin, ^{14}C-diuron, ^{14}C-2,4-D, ^{14}C-methyl parathion, ^{14}C-dieldrin ^{14}C-carbofuran	Soil, humic acid humin, corn, radishes	Methanol	27
Diuron, linuron, 3,4-dichloroaniline	Sassafras soil	Carbon dioxide with modifiers (methanol, ethanol, acetonitrite)	28
PAHs, phenols, aromatic carboxylic acids, pyrones, lipids	Quartz wool	Carbon dioxide	31

(continued)

TABLE 4. Continued

Compound	Matrix	SCF	Reference
DDT	Soils	Carbon dioxide, carbon dioxide with modifiers (methanol, toluene)	35
Organics	Chinese Maoming oil shale	Water, toluene	37
Sulfonyl urea herbicides and metabolites	Soil, plant materials, cell culture medium	Carbon dioxide with 2 percent methanol	40
Anthraquinone	Paper and pine plywood sawdust	Carbon dioxide	41
Polar compounds containing nitrogen and sulfur	Diesel fuel, marine sediments	Ammonia	44
PAHs, PCBs, heterocyclic organics	Urban dust (SRM-1649) river sediment, cigarette ash, lampblack	Carbon dioxide, nitrous oxide	48
α-Pinene camphene cineole, camphor, borneol, bornyl acetate, humulene	Spices, chewing gum, orange peel, spruce needles, cedar wood	Carbon dioxide	49
Phenolic compounds Resin and fatty acids	Wood, pine waxes	Carbon dioxide, propane, nitrous oxide, ethylene, acetone, methanol	70
Not specified	Lemon peel oil	Carbon dioxide	84
Simazine, atrazine, propazine, terbutylazine, cyanazine	Sediment	Carbon dioxide	120

(continued)

TABLE 4. Concluded

Compound	Matrix	SCF	Reference
PCBs	Sediments	Carbon dioxide, carbon dioxide with 2 percent methanol	121
2,3,7,8-TCDD	Sediments	Carbon dioxide, nitrous oxide, dioxide with 2 percent methanol, nitrous oxide with 2 percent methanol	122
PCBs, PAHs, S-containing herocyclic compounds, and n-alkanes	Polyurethane foam	Carbon dioxide	124
Polychlorinated dibenzo-p-dioxins and dibenzofurans	Municipal incinerator fly ash	Carbon dioxide, carbon dioxide with 10 percent benzene, nitrous oxide	125

345 atm. The SCF was depressurized through a combination of capillary-column and packed-column collector restrictors. The extracted materials were deposited onto a C_{18}-bonded-phase packed column. Compounds were eluted from the collector column with methylene chloride. No breakthrough was found on a second packed collector column placed in series with the first column.

The extraction efficiencies for PCBs from sediments and for PAHs from urban particulate matter were compared with Soxhlet extraction efficiencies. The data showed that comparable amounts of PCBs were extracted from sediments using Soxhlet or SFE techniques (Table 5). However, SFE provided higher recoveries than Soxhlet extraction for several PAHs (e.g., indeno(1,2,3-c,d)pyrene and benzo(g,h,i)perylene) from urban particulate material. Other PAHs were in good agreement (Table 6). Reextraction of the urban particulate material sample with SCF indicated complete removal of PAHs during the primary SFE step, and Soxhlet extraction of the urban particulate material, after extraction with SCF, also indicated complete removal of PAHs during the primary extraction.

The solubilizing properties of supercritical carbon dioxide were reported to be comparable to those of hexane (26) and benzene (125), but polar modifiers such as acetone or methanol, when added to the carbon dioxide, improved both solvent strength and selectivity. For example, Dobbs et al. (34) reported that the solubility of certain solids was increased markedly in supercritical carbon dioxide when small amounts of certain polar cosolvents were added. For 2-aminobenzoic acid, the addition of only 3.5 mole-percent methanol increased the solubility by 620 percent. The effect of adding various cosolvents to carbon dioxide on the solubility of benzoic acid is shown in Figure 27. The authors concluded that a nonpolar SCF, when doped with a small amount of certain cosolvents, can become highly selective.

Examples of cosolvent-induced solubility enhancement are shown in Table 7. In the case of benzoic acid, the solubility enhancement was significantly greater for methanol than for acetone. The same was true for 2-aminobenzoic acid. n-Octane gives an enhancement that is comparable to that of acetone due to the large degree of dispersion (34). Dobbs et al. suggested that most of the cosolvent-induced solubility enhancement can be explained by the dispersion and acid-base solubility parameters of the solute and cosolvent (34).

Dooley et al. (35) have studied the use of methanol and toluene as entrainers in the SFE of soils contaminated with hazardous organic compounds. Their results (Figure 28) show that the use of supercritical carbon dioxide with 5 wt-percent methanol is much more effective than the use of supercritical carbon dioxide with 5 wt-percent toluene.

McNally and Wheeler (28) reported that the extraction efficiencies for organics from soils can be predicted from packed-column SFC retention time data. Experiments performed with no modifier in the supercritical

TABLE 5. CONCENTRATION OF AROCLOR-1254 IN SEDIMENT

	Aroclor-1254 concentration (µg/g)[a]	
Extraction no.	Soxhlet extraction	SFE
1	6.61 ± 0.21	6.84 ± 0.18
2	6.71 ± 0.16	6.61 ± 0.19

[a] Data are given as average values ± S.D. Data are taken from Reference 19.

TABLE 6. CONCENTRATION OF SELECTED PAHs IN NIST SRM-1649

Extraction no.	Certified value	SFE[a]
Fluoranthene	7.1 ± 0.5	7.2 ± 0.1
Benz(a)anthracene	2.6 ± 0.3	2.3 ± 0.2
Benzo(a)pyrene	2.9 ± 0.5	3.1 ± 0.1
Benzo(g,h,i)perylene	4.5 ± 1.1	5.3 ± 0.5
Indeno(1,2,3-c,d)pyrene	3.3 ± 0.5	4.3 ± 0.1

[a] Data are given as average value ± S.D. (taken from Reference 19).

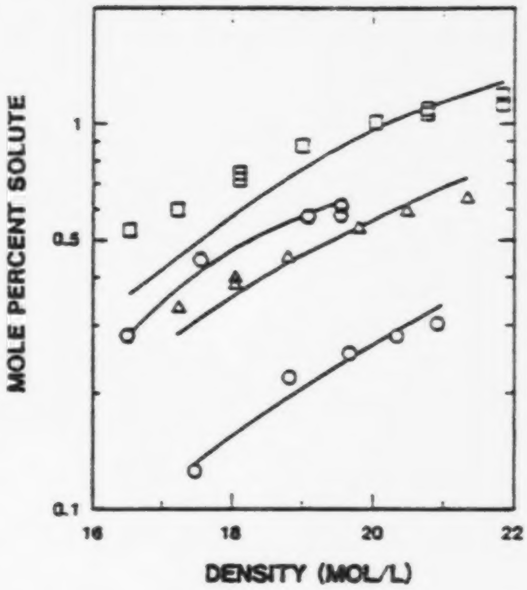


Figure 27. Solubility of benzoic acid in carbon dioxide with 3.5 mol-percent cosolvent at 35°C: (○) pure carbon dioxide, (Δ) acetone + carbon dioxide (□) methanol + carbon dioxide (O) n-octane + carbon dioxide (taken from Reference 34).

TABLE 7. COSOLVENT-INDUCED SOLUBILITY ENHANCEMENTS OF SOLIDS IN CARBON DIOXIDE AT 35°C AND AT A DENSITY OF 20.5 g-mol/L[a]

Solid	Cosolvent	y_2(ternary)/ y_2(binary)
Benzoic acid	Methanol	3.7
	Acetone	2.1
	n-Octane	2.3
2-Aminobenzoic acid	Methanol	7.2
	Acetone	3.1
Phthalic anhydride	Acetone	1.7
Hexamethylbenzene	Methanol	1.1
	Acetone	1.2
	n-Octane	2.1
	n-Pentane	1.8
Acridine	Methanol	2.3
	Acetone	1.7
2-Naphthol	Methanol	4.5

[a] Data taken from Reference 34. The carbon dioxide was doped with 3.4 mole-percent cosolvent.

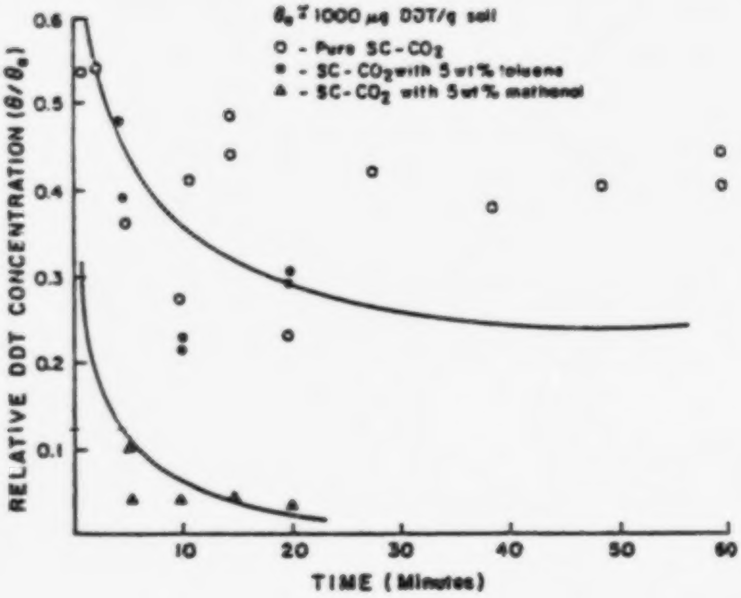


Figure 28. Temporal variation of relative soil concentration in the extraction of a DDT-contaminated, spill-site topsoil, showing the effect of entrainers (taken from Reference 35).

carbon dioxide showed that recoveries of diuron from sassafras soil were less than 10 percent. When 1.25 percent and 10 percent methanol were added, the cumulative recoveries were 4 percent and 81 percent, respectively. Irreproducible results were obtained when methanol concentrations exceeded 20 percent; this was attributed to the fact that because methanol solubility in carbon dioxide varies with temperature, it could be possible that the mixture of supercritical carbon dioxide with methanol may not have been homogeneous.

McNally and Wheeler also evaluated acetonitrile as modifier (28) because its dielectric constant is about 15 percent higher than that of methanol (38.8 versus 33.6). The extraction recoveries of diuron from sassafras soil with supercritical carbon dioxide and acetonitrile as modifier were lower (69 percent versus 81 percent for methanol).

Walsh, Ikonomou, and Donohue (51) presented a detailed study on the entrainer effect (i.e., the increase in both solvent power and selectivity) when a certain cosolvent is added to a SCF. They concluded that for many systems, the increase in the solvent power is due to an increase in the density of the solvent mixture. This effect is comparable to the effect which can be obtained with the pure solvent through manipulations of temperature and pressure.

The increase in the solventing power of a SCF containing an entrainer has been also reported by Paulitis et al. (14), Schmitt and Reid (45), and Van Alsten et al. (87). The study by Schmitt and Reid (45) addressed the effects of concentration and functionality of the entrainer, whereas Van Alsten's study addressed primarily the analyte functionality. Schmitt and Reid (45) experimented with four entrainers (benzene, cyclohexane, acetone, and methylene chloride) and two SCFs (carbon dioxide and ethane) and measured the solubilities of phenanthrene and benzoic acid in each SCF-entrainer combination. Van Alsten et al. (87) determined the solubilities of five compounds (phenanthrene, fluorene, fluorenone, dibenzofuran, and acridine) in pure carbon dioxide and carbon dioxide with 5 percent methanol. Van Alsten et al. (87) reported a significant increase in solubility for acridine with methanol as entrainer. Schmitt and Reid (45) reported a significant positive entrainer effect for benzoic acid only. Walsh et al. (51) attributed the enhancement effect reported by both Van Alsten et al. and Schmitt and Reid to the formation of Lewis acid-base complexes between analyte and entrainer. The enhancement factor for acridine was explained by the affinity of the Lewis acid methanol (pK_a 16) to the strong Lewis base acridine (pK_b 3.35). Likewise, the high enhancement factor for benzoic acid (pK_a 4.2) was explained by the strong Lewis-base action of acetone (pK_b 21.2) in the supercritical ethane (51). Furthermore, it was concluded that in the case of fluorenone/carbon dioxide/methanol, carbon dioxide competes with fluorenone to form hydrogen bonds with methanol, and, because carbon dioxide is in excess, there is no positive entrainer effect.

McDonald, Howard, and Bennett (70) have used supercritical propane, nitrous oxide, carbon dioxide, and ethylene to extract resin and fatty acids from southern pine, and wax from Douglas-fir bark. Their results are shown in Table 8. Propane gave the highest yields: 18.8 percent yield of resin acids and 5.5 percent yield of wax. The weight of extracted material was greater using SCFs than using a comparable weight of petroleum ether; furthermore, the extraction time was shorter. Therefore, SCFs could replace petroleum-based solvents for the extraction of chemicals from wood.

Funazukuri and Wakao (37) have studied the SFE of Chinese Maoming oil shale with water and toluene. Their results show that more organic components of high molecular weight were extracted with supercritical toluene than with supercritical water, although the total weight loss of the oil shale sample was almost the same in both cases. The extraction of average-molecular-weight compounds and the total amount of oil extracted was represented by the order - supercritical toluene > supercritical water > Soxhlet extraction with tetrahydrofuran. The extracts obtained with supercritical toluene and supercritical water had almost the same yield distribution of n-alkanes.

Hawthorne and Miller (25, 26, 49) used SCFs (carbon dioxide, nitrous oxide) to extract polycyclic aromatic hydrocarbons (PAHs) from 20-mg samples of urban dust and 50-mg samples of fly ash and river sediment. They reported that nitrous oxide with 5 percent methanol gave the best recoveries. The recoveries of various PAHs from 30- and 60-min extractions with nitrous oxide are shown in Table 9. Figure 29 shows the recoveries of PAHs from urban dust, fly ash, and river sediment using five different SCFs.

The use of SCFs for the extraction of semivolatile and higher-molecular-weight organic compounds from various adsorbent and particulate matrices was investigated by Smith et al. (20, 21, 42, 44, 47). Supercritical carbon dioxide, isobutane, and methanol-modified carbon dioxide were used for sample extraction. SFE provided rapid extractions, with efficiencies comparable to those obtained with the Soxhlet method. Polar compounds were extracted more efficiently with supercritical carbon dioxide containing methanol as modifier, whereas isobutane was found to be more efficient for the higher-molecular-weight and less-polar compounds. Results of the extraction comparison of XAD-2 resin, polyurethane foam, and Spherocarb using Soxhlet extraction and extraction with various SCFs are shown in Tables 10, 11, and 12, respectively. While the data in Tables 10 and 11 are self-explanatory, the data in Table 12 are worth discussing. With Soxhlet extraction, recoveries of the five test compounds from Spherocarb were below 5 percent. Supercritical carbon dioxide extraction did not recover any of the target compounds whereas supercritical isobutane and methanol-modified carbon dioxide recovered very small quantities. Soxhlet extraction of the Spherocarb material after the SFE recovered only trace amounts of chrysene and coronene.

Other compounds extracted from soil, sediment, and fly-ash samples with supercritical carbon dioxide include several triazine herbicides (120)

TABLE 8. COMPARISON OF EXTRACT YIELDS FROM SOUTHERN PINE BY SFE AND SOLVENT EXTRACTION[a]

	Time	Weight of extractant	Extract yield	Amount extracted
Extractant	hr	g Extractant/ g dry wood	As percentage of dry wood	mg Extract/ 100 g extractant
Petroleum ether[b] (30-60°C)	6	550	12	22
	40	2,490	18	7.2
Propane (21 MPa)	3	6[c]	19	3,250
Nitrous oxide (21 MPa)	0.25	8[c]	6.8	860
Ethylene (21 MPa)	0.25	5[c]	2.3	460
Carbon dioxide (21 MPa)	0.25	8[c]	2.1	270

[a] Data taken from Reference 70.

[b] Soxhlet exttraction at 6 cycles/hr, 40 g petroleum ether/cycle; dry weight of sample, 2.5 g.

[c] Dry weight of sample, 19 g.

TABLE 9. RECOVERIES OF PAHs FROM URBAN DUST (SRM 1649) USING SUPERCRITICAL NITROUS OXIDE/5 PERCENT METHANOL[a]

Compound	Concentration (µg/g)		
	Certified value[b]	30-min extraction	60-min extraction
Fluoranthene (202)[c]	7.1 ± 0.5	7.4 ± 0.4	8.0 ± 0.6
Benz(a)anthracene (228)	2.6 ± 0.3	2.5 ± 0.3	2.9 ± 0.5
Benzo(a)pyrene (252)	2.9 ± 0.5	2.9 ± 0.2	3.2 ± 0.3
Benzo(g,h,i)perylene (276)	4.5.± 1.1	3.2 ± 0.3	4.4 ± 0.3
Indeno(1,2,3-c,d)pyrene (276)	3.3 ± 0.5	2.3 ± 0.2	3.1 ± 0.2

[a] Data taken from Reference 26.

[b] Values as certified by the National Institute of Standards and Technology.

[c] The numbers in parentheses are the molecular weights of the compounds.

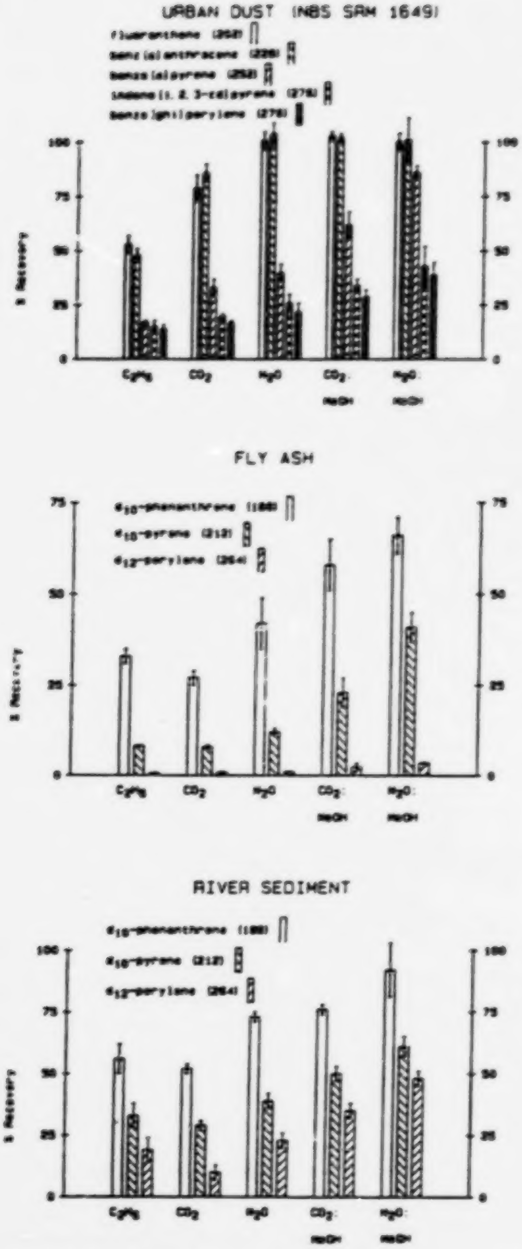


Figure 29. Comparison of PAH extraction efficiencies obtained for urban dust (National Institute of Standards and Technology SRM 1649), fly ash, and river sediment using five different SCFs: ethane, carbon dioxide, nitrous oxide, carbon dioxide with 5 percent methanol modifier, and nitrous oxide with 5 percent methanol modifier. Error bars represent one standard deviation unit for triplicate extractions of each sample with each solvent. Extraction and analysis conditions are given in Reference 26.

TABLE 10. EXTRACTION COMPARISON OF XAD-2 RESIN USING SOXHLET AND SFE[a]

		Percent recovery					
		Carbon dioxide[c]		Isobutane[d]		Carbon dioxide/ methanol[e]	
Compound	Soxhlet only[b]	SFE	Soxhlet[f]	SFE	Soxhlet[f]	SFE	Soxhlet[f]
Chrysene	79	84	0	86	5	88	3
Benzanthrone	86	98	0	110	0	88	0
1-Nitropyrene	93	81	0	70	0	98	0
Dibenzo(a,i)carbazole	88	54	22	96	6	97	0
Coronene	81	46	63	93	9	90	5
Decacyclene	85	6	88				

[a] Data taken from Reference 21.

[b] Methylene chloride for 16 hr.

[c] Carbon dioxide at 125°C and 400 bar with approximately 200 mL of liquid.

[d] Isobutane at 150°C and 185 bar with approximately 300 mL of liquid.

[e] Twenty mole-percent methanol in carbon dioxide at 130°C and 400 bar with approximately 210 mL of liquid.

[f] Soxhlet extraction of same sample (after SFE) using methylene chloride.

TABLE 11. EXTRACTION COMPARISON OF POLYURETHANE FOAM USING SOXHLET AND SFE[a]

	Percent recovery						
		Carbon dioxide[c]		Isobutane[d]		Carbon dioxide/ methanol[e]	
Compound	Soxhlet only[b]	SFE	Soxhlet[f]	SFE	Soxhlet[f]	SFE	Soxhlet[f]
Chrysene	95	88	0	94	0	97	5
Benzanthrone	86	92	0	101	0	102	0
1-Nitropyrene	82	70	0	54	21	33	3
Dibenzo(a,i)carbazole	76	70	14	51	15	93	7
Coronene	85	82	14	78	6	80	4
Decacyclene		6	92				

[a] Data taken from Reference 21.

[b] Methylene chloride for 16 hr.

[c] Carbon dioxide at 125°C and 400 bar with approximately 163 mL of liquid.

[d] Isobutane at 150°C and 185 bar with approximately 125 mL of liquid.

[e] Twenty mole-percent methanol in carbon dioxide at 130°C and 400 bar with approximately 120 mL of liquid.

[f] Soxhlet extraction of same sample (after SFE) using methylene chloride.

TABLE 12. EXTRACTION COMPARISON OF SPHEROCARB USING SOXHLET AND SFE[a]

		Percent recovery					
		Carbon dioxide[c]		Isobutane[d]		Carbon dioxide/ methanol[e]	
Compound	Soxhlet only[b]	SFE	Soxhlet[f]	SFE	Soxhlet[f]	SFE	Soxhlet[f]
Chrysene	5	0	1	2	2	2	0
Benzanthrone	4	0	0	11	0	3	0
1-Nitropyrene	0	0	0	0	0	0	0
Dibenzo(a,i)carbazole	0	0	0	3	2	3	0
Coronene	1	0	2	4	3	3	2

[a] Data taken from Reference 21.

[b] Methylene chloride for 16 hr.

[c] Carbon dioxide at 125°C and 400 bar with approximately 215 mL of liquid.

[d] Isobutane at 150°C and 185 bar with approximately 400 mL of liquid.

[e] Twenty mole-percent methanol in carbon dioxide at 130°C and 400 bar with approximately 214 mL of liquid.

[f] Soxhlet extraction of same sample (after SFE) using methylene chloride.

and polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) (122, 125). The triazine herbicides were extracted from 0.5-g spiked sediment samples with carbon dioxide at 230 bar and 48°C (120). Recoveries of propazine, terbutylazine, atrazine, and cyanazine were quantitative (82.4 to 96.4 percent); the simazine recoveries were only 42.5 percent. Addition of 20 µL methanol to the 0.5-g sediment sample increased the recovery of simazine to 92.0 percent. The PCDDs and PCDFs were extracted quantitatively from 0.8-g fly-ash samples with nitrous oxide at 400 atm and 40°C. Supercritical carbon dioxide did not extract the PCDDs, and only small amounts of PCDFs were found in the extraction mixture; however, supercritical carbon dioxide modified with 10 percent benzene was reported to extract the PCDDs and PCDFs quantitatively (125).

4.2 EFFECT OF TEMPERATURE/PRESSURE/FLOWRATE

Figure 30 shows three capillary gas chromatograms of polycyclic aromatic fractions obtained by supercritical carbon dioxide extraction of a coal tar sample at 50°C and 80, 125, and 200 atm (20). The peaks labelled A and B refer to the same respective components in each fraction and were arbitrarily chosen to serve as reference points to facilitate comparison. This example clearly demonstrates that as the pressure increased, more higher-molecular-weight organics were extracted from the sample. The components in the extract obtained at 80 atm pressure consisted primarily of two-ring, alkylated two-ring, three-ring, and some lower-alkylated three-ring compounds. The 125-atm extract consisted predominantly of alkylated three-ring, four-ring, and some alkylated four-ring structures, and the 200-atm extract consisted primarily of alkylated four-ring and larger structures.

The effect of pressure on the use of supercritical carbon dioxide for extraction was investigated by Stahl et al. (31). The compounds selected differ in their molecular weights and in the numbers and natures of chemical functionalities. Stahl's findings are summarized below:

- Hydrocarbons and other lipophilic organic compounds of relatively low polarity (e.g., esters, ethers, lactones, epoxides) can be extracted in the lower pressure range (70 to 100 atm).
- More strongly polar substances (e.g., sugars, amino acids) cannot be extracted below 500 atm.
- The introduction of strongly polar functional groups (e.g., hydroxyl, carboxyl) makes the extraction more difficult. Compounds with three hydroxyls or one carboxyl and two hydroxyl groups can be extracted. Aromatic compounds with one carboxyl and three hydroxyl groups cannot be extracted.

The effect of temperature on the extraction of organics from contaminated soil was investigated by Dooley et al. (35). These authors reported that increasing the temperature will lower the solubility of

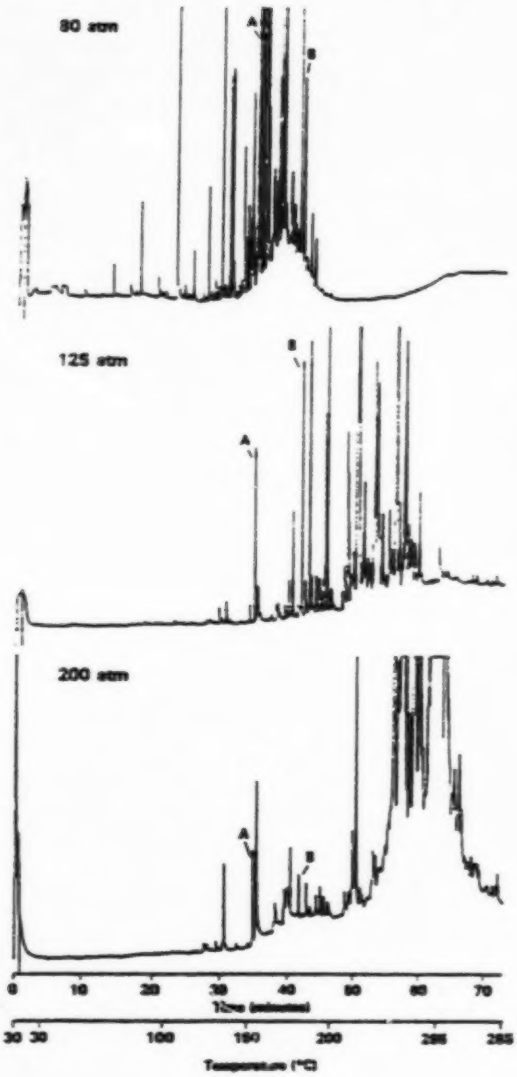


Figure 30. Capillary gas chromatograms of PAH fractions obtained from the supercritical carbon dioxide extraction of a coal tar sample at various pressures (taken from Reference 20).

TABLE 13. CONCENTRATION OF DDT IN SPILL-SITE TOPSOIL EXTRACTED BY SFE: EFFECT OF TEMPERATURE[a]

	Concentration (ppm)	
Extraction time (min)	Supercritical carbon dioxide-toluene	Supercritical carbon dioxide-methanol
Conditions: 40°C, 100 atm, 315 cm^3/s at 25 percent modifier, 1 atm		
0	1,271	1,271
5	507, 597, 612	132, 59, 55
10	272, 280	59, 67
20	416, 416	51, 45
30	401	
Conditions: 80°C, 100 atm, 315 cm^3/s at 25 percent modifier, 1 atm		
0	1,271	1,271
5	1,133	965
10	675, 722	805, 716
20	465	

[a] Data are taken from Reference 35. Multiple entries in concentration columns pertain to replicate analyses.

compounds in supercritical carbon dioxide. Data presented in Table 13 show that raising the extraction temperature from 40°C to 80°C reduces the rate of extraction. In order to determine the rate-limiting step in the extraction, Dooley et al. (35) carried out extractions at various flow rates while maintaining the constant level of entrainer in the SCF. Their results (Table 14) indicate that the extraction process is not limited by external mass transfer. This is contrary to what McNally and Wheeler (28) reported for diuron and linuron using packed-column SCF chromatography. In the case of diuron, the highest recovery was obtained at 100°C, the lowest at 55°C (28). The first 15 min of each extraction yielded the highest recoveries (61 percent at 100°C and 47 percent at 75°C). A leveling in the amount was observed in less than 1 hour in both cases. Increasing the pressure also increased the extraction efficiency of diuron. Furthermore, it was reported that a pressure increase at 75°C increased the extraction efficiency more than a similar increase at 100°C (28).

4.3 SAMPLE COLLECTION

Collection of organics during the depressurization process has been done by trapping the extraction effluent either in the bulb of an open 100-mL volumetric flask cooled to 0°C, or in a sealed container that is cooled in liquid nitrogen (42). The former is less desirable because the more volatile compounds can be lost through solute aerosol formation (Table 15). The increased recoveries for the carbon dioxide-methanol combination was attributed to the formation of relatively large methanol droplets which contained the analytes (Table 16).

Sugiyama and Saito (84) used a 250-mm x 0.25-mm ID stainless-steel tube as a flow restrictor. The restrictor tube was crimped to increase the flow resistance. The pressure of the fluid containing the extract was released as it flowed through the restrictor, and the extract was collected in a 200-μL microvial kept at room temperature. Lemon peel oil was extracted with sub- and supercritical carbon dioxide at various pressures and temperatures, and the results were compared to those for a cold-pressed lemon oil.

Another way to collect organic compounds removed from a solid sample by a SCF is to trap them on an adsorbent material. Schantz and Miller (19) used a stainless-steel tube (5 cm x 6.35 mm OD), packed with μBondapak C_{18}/Corasil, attached to the end of a capillary restrictor (66-cm x 60-μm ID fused-silica capillary). The capillary served to reduce the carbon dioxide pressure to atmospheric pressure. Removal of the organics collected on the C_{18} column was achieved by connecting the column to a high-pressure liquid chromatograph and eluting it with methylene chloride.

The ID of the restrictor is very critical when the SFE is done on-line with a chromatographic technique. Hawthorne and Miller (26) reported that use of restrictors with internal diameters larger than 30 μm was impractical for direct GC/MS analysis because the resulting high flow rates

TABLE 14. CONCENTRATION OF DDT IN SPILL-SITE TOPSOIL EXTRACTED BY SFE WITH SUPERCRITICAL CARBON DIOXIDE-METHANOL: EFFECT OF FLOWRATE[a]

	Concentration (ppm)	
Extraction time (min)	Flowrate 470 cm^3/s	Flowrate 47 cm^3/s
Conditions: 40°C, 100 atm, 470 and 47 cm^3/s		
0	1,271	1,271
1	207, 221, 222, 236	
2	82, 95, 96, 105	
5	58, 61, 66	60
10	37, 52	
20		86
40		34
60		51
120		25

[a] Data are taken from Reference 35. Multiple entries in concentration column are replicate analyses.

TABLE 15. COMPARISON OF EXTRACTION RECOVERIES FROM XAD-2 RESIN[a] USING DIFFERENT COLLECTION METHODS[a]

	Percent recovery	
Compound	Open collection[b]	Sealed collection[c]
Chrysene	2.2	75
Benzanthrone	2.5	79
1-Nitropyrene	1.8	83
Dibenzo(a,i)carbazole	6.3	95
Coronene	8.2	81
Rubrene	0	25

[a] Extraction conditions: carbon dioxide at 150°C and 410 bar. Data are taken from Reference 42.

[b] Open collection in a narrow-necked flask at 0°C, no solvent.

[c] Sealed collection in a flask, cooled with liquid nitrogen, no solvent.

[d] Data are taken from Reference 42.

TABLE 16. COMPARISON OF EXTRACTION RECOVERIES FROM XAD-2 USING OPEN COLLECTION AND VARIOUS EXTRACTION CONDITIONS[a]

Compound	Percent recovery Carbon dioxide (150°C)	Carbon dioxide (50°C)	Carbon dioxide/methanol[b] (150°C)
Chrysene	2.2	25	60
Benzanthrone	2.5	28	62
1-Nitropyrene	1.8	24	29
Dibenzo(a,i)carbazole	6.3	10	65
Coronene	8.2	6.5	62

[a] Extractions were conducted at 410 bar. Data are taken from Reference 42.
[b] Twenty mole-percent methanol.

could not be maintained by the pumping system. Recoveries of various PAHs from river sediment were quantitative when a 25-μm restrictor was employed; however, in the case of fly ash the extraction recoveries were much lower, even when the extraction was performed for 60 min (Table 17).

The relationship between the inner diameter of the restrictor and the quality of chromatography for SFE coupled to a gas chromatograph was investigated by Hawthorne and Miller (48) using a river sediment sample spiked with 0.5 mg/g of a coal-derived anthracene oil which contained primarily PAHs. The results are presented in Figure 31. It was concluded that use of 25-μm ID restrictors yields good chromatographic peak shapes when a 30-m x 0.32-mm ID (1.0-μm film thickness) column is used for analysis. With restrictors of internal diameters <15 μm, the extraction time was three times as long as for the 25-μm restrictor (48). When a 30-μm restrictor was used with a wide-bore column, the peak shape began to degrade, particularly for early eluting compounds, and peak splitting was reported on a narrow-bore column.

TABLE 17. RECOVERY OF PAH FROM RIVER SEDIMENT AND FLY ASH USING SUPERCRITICAL NITROUS OXIDE/5 PERCENT METHANOL[a]

Compound	Percent recovery		
	25-μm restrictor		30-μm restrictor 60 min
	30 min	60 min	
River Sediment			
Phenanthrene-d_{10} (188)[b]	102 ± 4	103 ± 7	
Pyrene-d_{10} (212)	95 ± 2	101 ± 8	
Perylene-d_{12} (264)	92 ± 10	97 ± 6	
Fly Ash			
Phenanthrene-d_{10} (188)	72 ± 5	89 ± 8	102 ± 6
Pyrene-d_{10} (212)	48 ± 8	57 ± 4	74 ± 8
Perylene-d_{10} (264)	19 ± 5	28 ± 5	44 ± 9

[a] Data are taken from Reference 26.

[b] The numbers in parentheses are the molecular weights of the compounds.

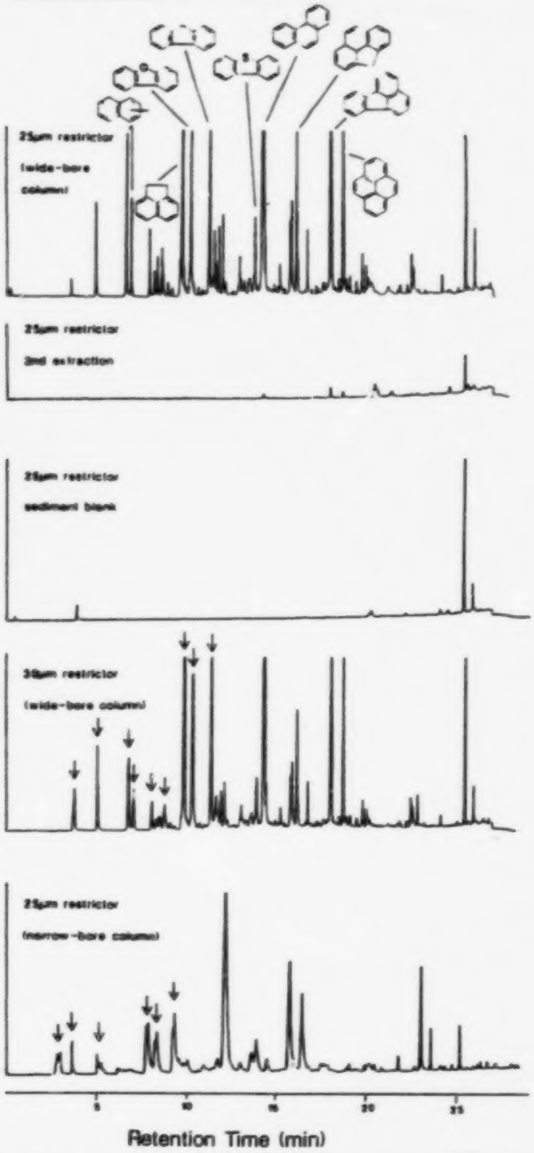


Figure 31. Coupled SFE-GC/FID analysis of river sediment that had been spiked with a coal-derived anthracene oil. The top three chromatograms were generated using a 25-μm ID restrictor with a wide-bore (0.32-mm ID) chromatographic column; they show two consecutive SFE-GC-FID analyses of the same sample, and an analysis of the unspiked sediment (sediment blank). The bottom two chromatograms show the degradation in chromatographic peak shape that occurred when the restrictor ID was increased to 30 μm (with the wide-bore column) and when a 25-μm ID restrictor was coupled with a narrow-bore column (taken from Reference 48).

REFERENCES

1. McHugh, M. A., and V. J. Krukonis, Supercritical Fluid Extraction: Principles and Practice, Butterworth Publishers (1986).

2. Penninger, J. M. L., M. Radosz, M. A. McHugh, and V. J. Krukonis, Eds., Supercritical Fluid Technology, Elsevier, Amsterdam (1985).

3. Charpentier, B. A., and M. R. Sevenants, Eds., Supercritical Fluid Extraction and Chromatography: Techniques and Applications. ACS Symposium Series 366 (1988).

4. Squires, T. G., and M. E. Paulaitis, Eds., Supercritical Fluids: Chemical and Engineering Principles and Applications, ACS Symposium Series 329 (1987).

5. Francis, A. W., "Ternary Systems of Liquid Carbon Dioxide", J. Phys. Chem. 58, 1099-1114 (1954).

6. Fluid Phase Equil. 10, 135-354 (1983).

7. Schneider, G. M., E. Stahl, and G. Wilke, Eds., Extraction with Supercritical Gases, Verlag Chemie, Deerfield Beach, FL (1980).

8. Paul, P. M. F., and W. S. Wise, The Principles of Gas Extraction, Mills and Boon, London (1971).

9. Irani, C. A., and E. W. Funk, "Separations Using Supercritical Gases," in Recent Developments in Separation Science, Vol. 3, Part A, CRC Press, Boca Raton, FL, 171-177 (1977).

10. Gangoli, N., and G. Thodes, "Liquid Fuels and Chemical Feedstocks from Coal by Supercritical Gas Extraction," Ind. Eng. Chem. Prod. Res. Dev. 16, 208-216 (1977).

11. William, D. F., "Extraction with Supercritical Gases," Chem. Eng. Sci. 36, 1769-1788 (1981).

12. Brunner, G., and S. Peter, "Zum Stand der Extraktion mit Komprimierten Gasen," Chem. Ing. Tech. 53, 529-542 (1981).

13. Paulaitis, M. E., J. M. L. Penninger, R. D. Gray, and P. Davidson, Eds., Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor Science, Ann Arbor, MI (1983).

(212)

14. Paulaitis, M. E., V. J. Krukonis, R. T. Kurnik, and R. C. Reid, "Supercritical Fluid Extraction," *Rev. Chem. Eng.* 1, 179-250 (1982).

15. McHugh, M. A., "Extraction with Supercritical Fluids," in *Recent Developments in Separation Science*, Vol IX, Li, N. N., and J. M. Calo, Eds., Boca Raton, FL, 75-105 (1986).

16. Randall, L. G., "The Present Status of Dense (Supercritical) Gas Extraction and Dense Gas Chromatography: Impetus for DGC/MS Development," *Sep. Sci. Technol.* 17, 1-118 (1982).

17. Johnson, K. P., "Supercritical Fluids," in *Encyclopedia of Chemical Technology*, 3rd Ed., Suppl. Vol., John Wiley & Sons, NY, 872-893 (1984)

18. Brady, B. O., C. P. C. Kao, K. M. Dooley, F. C. Knopf, and R. P. Gambrell, "Supercritical Fluid Extraction of Toxic Organics from Soils," *Ind. Eng. Chem. Res.* 26, 261-268 (1987).

19. Schantz, M. M., and S. N. Chesler, "Supercritical Fluid Extraction Procedure for the Removal of Trace Organic Species from Solid Samples," *J. Chrom.* 363, 397-401 (1986).

20. Wright, B. W., S. L. Frye, D. G. McMinn, and R. D. Smith, "Online Supercritical Fluid Extraction-Capillary Gas Chromatography," *Anal. Chem.* 59, 640-644 (1987).

21. Wright, B. W., C. W. Wright, R. W. Gale, and R. D. Smith, "Analytical Supercritical Fluid Extraction of Adsorbent Materials," *Anal. Chem.* 59, 38-44 (1987).

22. Smith, R. D., and H. R. Udseth, "Direct Mass Spectrometric Analysis of Supercritical Fluid Extraction Products," *Sep. Sci. Technol.* 16, 112, 18(3), 245-252 (1983).

23. Jinno, K., T. Hoshino, T. Hondo, M. Saito, and M. Senda, "Identification of Polycyclic Aromatic Hydrocarbons in Extracts of Diesel Particulate Matter by Supercritical Fluid Chromatography Coupled with an Ultraviolet Multichannel Detector," *Anal. Chem.* 58, 2696-2699 (1986).

24. Raymer, J. H., E. D. Pellizzari, and S. D. Cooper, "Desorption Characteristics of Four Polyimide Sorbent Materials Using Supercritical Carbon Dioxide and Thermal Methods," *Anal. Chem.* 59, 2069-2073 (1987).

25. Hawthorne. S. B., and D. J. Miller, "Extraction and Recovery of Organic Pollutants from Environmental Solids and Tenax-GC Using Supercritical CO_2," *J. Chrom. Sci.* 24, 258-264 (1986).

26. Hawthorne, S. B., and D. J. Miller, "Extraction and Recovery of Polycyclic Aromatic Hydrocarbons from Environmental Solids Using Supercritical Fluids," Anal. Chem. 59, 1705-1708 (1987).

27. Capriel P., A. Haisch, and S. U. Khan, "Supercritical Methanol: An Efficacious Technique for the Extraction of Bound Pesticide Residues from Soil and Plant Samples," J. Agric. Food Chem. 34, 70-73 (1986).

28. McNally, M.E.P., and J. R. Wheeler, "Increasing Extraction Efficiency in Supercritical Fluid Extraction from Complex Matrices," J. Chrom. 447, 53-63 (1988).

29. Skelton, Jr., R. J., C. C. Johnson, and L. T. Taylor, "Sampling Considerations in Supercritical Fluid Chromatography," Chromatographia 21, 3-8 (1986).

30. Finn, M. J., C. J. Bower, and R. D. Hughes, "The Extraction of Coal with Supercritical Hydrocarbon Mixtures," Fluid Phase Equil. 10, 327-336 (1983).

31. Stahl, E., W. Schutz, E. Schutz, and E. Willing, "A Quick Method for the Microanalytical Evaluation of the Dissolving Power of Supercritical Gases," Angew. Chem. Int. Ed. Engl. 17, 731-738 (1978).

32. Picht, R. D., T. R. Dillman, D. J. Burke, and R. P. deFilippi, "Regeneration of Adsorbents by a Supercritical Fluid," in Adsorption and Ion Exchange, AIChE Symposium Series 219, 78, 136-149 (1982).

33. Dandge, D. K., J. P. Heller, and K. V. Wilson, "Structure Solubility Correlations: Organic Compounds and Dense Carbon Dioxide Binary Systems," Ind. Eng. Chem. Prod. Res. Dev. 24, 162-166 (1985).

34. Dobbs, J. M., J. M. Wong, R. J. Lahiere, and K. P. Johnston, "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvents," Ind. Eng. Chem. Res. 26, 56-65 (1987).

35. Dooley, K. M., C. P. Kao, R. P. Gambrell, and F. C. Knopf, "The Use of Entrainers in the Supercritical Extraction of Soils Contaminated with Hazardous Organics," Ind. Eng. Chem. Res. 26, 2058-2062 (1987).

36. Greenkorn, R. A., and K. C. Chao, "Supercritical Fluid Extraction of Coal," DOE Report PC/60036--15 (1987).

37. Funazukuri, T., and N. Wakao, "Supercritical Fluid Extraction of Chinese Maoming Oil Shale with Water and Toluene," Sadhana 10, 307-317 (1987).

38. Dobbs, J. M., and K. P. Johnston, "Selectivities in Pure and Mixed Supercritical Fluid Solvents," Ind. Eng. Chem. Res. 26, 1476-1482 (1987).

39. Berry, A. J., D. E. Gamer, and J. R. Perkins, "Supercritical Fluid Chromatographic and Supercritical Fluid Chromatographic-Mass Spectrometric Studies of Some Polar Compounds," J. Chrom. 363, 147-158 (1986).

40. McNally, M. E. P., and J. R. Wheeler, "Supercritical Fluid Extraction Coupled with Supercritical Fluid Chromatography for the Separation of Sulfonylurea Herbicides and Their Metabolites from Complex Matrices," J. Chrom. 435, 63-71 (1988).

41. Schneiderman, M. A., A. K. Sharma, and D. C. Locke, "Determination of Anthraquinone in Paper and Wood Using Supercritical Fluid Extraction and High-Performance Liquid Chromatography with Electrochemical Detection," J. Chrom. 409, 343-353 (1987).

42. Wright, B. W., and R. D. Smith, "Supercritical Fluid Extraction of Particulate and Adsorbent Materials: Part II," EPA Report 600/4-87/040 (1987).

43. Brignole, E. A., P. M. Andersen, and A. Fredenslund, "Supercritical Fluid Extraction of Alcohols from Water," Ind. Eng. Chem. Res. 26, 254-261 (1987).

44. Smith, R. D., H. R. Udseth, and R. N. Hazlett, "Diesel Fuel Marine and Sediment Analysis: Supercritical Ammonia Extraction and Direct Fluid Injection-Mass Spectrometry," Fuel 64, 810-815 (1985).

45. Schmitt, W. J., and R. C. Reid, "The Influence of the Solvent Gas on Solubility and Selectivity in Supercritical Extraction," in Supercritical Fluid Technology, Penninger, J. M. L., M. Radosz, M. A. McHugh, and V. J. Krukonis, Eds., Elsevier: Amsterdam, 124-147 (1985).

46. Ikushima, Y., K. Hatakeda, S. Ito, N. Saito, T. Asano, and T. Goto, "A Supercritical Carbon Dioxide Extraction from Mixtures of Triglycerides and Higher Fatty Acid Methyl Esters Using a Gas-Effusion-Type System," Ind. Eng. Chem. Res. 27, 818-823 (1988).

47. Smith, R. D., S. L. Frye, C. R. Yonker, and R. W. Gale, "Solvent Properties of Supercritical Xe and SF_6," J. Phys. Chem. 91, 3059-3062 (1987).

48. Hawthorne, S. B., and D. J. Miller, "Directly Coupled Supercritical Fluid Extraction-Gas Chromatographic Analysis of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls from Environmental Solids," J. Chrom. 403, 63-76 (1987).

49. Hawthorne, S. B., M. S. Krieger, and D. J. Miller, "Analysis of Flavor and Fragrance Compounds Using Supercritical Fluid Extraction Coupled with Gas Chromatography," Anal. Chem. 60, 472-477 (1988).

50. Brown, B. O., A. J. Kishbaugh, and M. E. Paulaitis, "Experimental Determination of Enhancement Factors from Supercritical-Fluid Chromatography," Fluid Phase Equil. 36, 247-261 (1987).

51. Walsh, J. M., G. D. Ikonomou, and M. D. Donohue, "Supercritical Phase Behaviour: The Entrainer Effect," Fluid Phase Equil. 33, 295-319 (1987).

52. Kumar, S. K., U. W. Suter, and R. C. Reid, "Fractionation of Polymers with Supercritical Fluids," Fluid Phase Equil. 29, 373-382 (1986).

53. Kalra, H., S. Y.-K. Chung, and C. J. Chen, "Phase Equilibrium Data for Supercritical Extraction of Lemon Flavors and Palm Oils with Carbon Dioxide," Fluid Phase Equil. 36, 263-278 (1987).

54. Prausnitz, J. M., R. N. Lichtenthaler, and E. G. de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria, 2nd Edition, Prentice-Hall, Englewood Cliffs, New Jersey (1986).

55. Rowlinson, J. S., and M. J. Richardson, "The Solubility of Solids in Compressed Gases," Advan. Chem. Phys. 2, 85-118 (1959).

56. Pitzer, K. S., and R. F. Curl, "The Volumetric and Thermodynamic Properties of Fluids. III. Empirical Equation for the Second Virial Coefficient," J. Am. Chem. Soc. 79, 2369-2370 (1957).

57. Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, The Properties of Gases and Liquids, 3rd Edn., McGraw Hill, NY (1977).

58. Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibria at High Pressures. Vapor-Phase Fugacity Coefficients in Nonpolar and Quantum-Gas Mixtures," Ind. Eng. Chem. Fundls. 6, 492-498 (1967).

59. Van Leer, R. A., and M. E. Paulaitis, "Solubilities of Phenol and Chlorinated Phenols in Supercritical Carbon Dioxide," J. Chem. Eng. Data 25, 257-259 (1980).

60. McHugh, M A., and M. E. Paulaitis, "Solid Solubilities of Naphthalene and Biphenyl in Supercritical Carbon Dioxide," J. Chem. Eng. Data 25, 326-329 (1980).

61. McHugh, M. A., A. J. Seckner, and T. J. Yogan, "High-Pressure Phase Behavior of Octacosane and Carbon Dioxide," Ind. Eng. Chem. Fundam. 23 493-499 (1984).

62. Eisenbach, W., "Supercritical Fluid Extraction: A Film Demonstration," Ber. Bunsenges. Phys. Chem. 88, 881-886 (1984).

63. deFilippi, R. P., and J. E. Vivian, "Process for Separating Liquid Solutes from Their Solvent Mixtures," U. S. Patent 4,349,415 (1982).

216

64. Wright, B. W., J. L. Fulton, A. J. Kopriva, and R. D. Smith, "Analytical Supercritical Fluid Extraction Methodologies," in *Supercritical Fluid Extraction and Chromatography: Techniques and Applications*, Charpentier, B. A., and M. R. Sevenants, Eds.; ACS Symposium Series 366, 44-62 (1988).

65. Kalinoski, H. T., H. R. Udseth, B. W. Wright, and R. D. Smith, "Supercritical Fluid Extraction and Direct Fluid Injection Mass Spectrometry for the Determination of Trichothecene Mycotoxins in Wheat Samples," *Anal. Chem.* 58, 2421-2429 (1986).

66. Unger, K. K., and P. J. Roumeliotis, "On-Line High Pressure Extraction-High-Performance Liquid Chromatography. I. Equipment Design and Operation Variables," *J. Chrom.* 282, 519-526 (1983).

67. Sugiyama, K., M. Saito, T. Hondo, and M. Senda, "New Double-Stage Separation Analysis Method: Directly Coupled Laboratory-Scale Supercritical Fluid Extraction-Supercritical Fluid Chromatography Monitored with a Multiwavelength Ultraviolet Detector," *J. Chrom.* 332, 107-116 (1985).

68. Modell, M., R. D. deFilippi, and V. J. Krukonis, "Regeneration of Activated Carbon with Supercritical Carbon Dioxide," *Ann. ACS Mtg.*, Miami (1978).

69. deFilippi, R. P., V. J. Krukonis, R. J. Robey, and M. Modell, "Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides," *EPA Report* 600/2-80-054, March (1980).

70. McDonald, E. C., J. Howard, and B. Bennett, "Chemicals from Forest Products by Supercritical Fluid Extraction," *Fluid Phase Equil.* 10, 337-344 (1983).

71. Larson, K. A., and M. L. King, "Evaluation of Supercritical Fluid Extraction in the Pharmaceutical Industry," *Biotech. Prog.* 2, 73-82 (1988).

72. Yilgor, I., J. E. McGrath, and V. J. Krukonis, "Novel Supercritical Fluid Techniques for Polymer Fractionation and Purification 1. Background; 2. Fractionation and Characterization of Functional Siloxane Oligomers," *Polym. Bull.* 12, 491-506 (1984).

73. Krukonis, V. J., "Processing of Polymers with Supercritical Fluids," *Polymer News* 11, 7-16 (1985).

74. Kumar, S. K., U. W. Suter, and R. C. Reid, "A Statistical-Mechanics Based Lattice Model Equation of State: Applications to Mixtures with Supercritical Fluids," *ACS Fuel Chemistry* 30, 66-77 (1985).

75. Randolph, T. W., H. W. Blanch, J. M. Prausnitz, and C. R. Wilke, "Enzymatic Catalysis in a Supercritical Fluid," *Biotech. Letters* 7, 325-328 (1985).

76. Hammond, D. A., M. Karel, A. M. Klibanov, and V. J. Krukonis, "Enzymatic Reactions in Supercritical Gases," Appl. Biochem. Biotech. 11, 393-400 (1985).

77. Taniguchi, M., M. Kamihira, and T. Kobayashi, "Effect of Treatment with Supercritical Carbon Dioxide on Enzymatic Activity," Agric. Biol. Chem. 51, 593-594 (1987).

78. Coenan, H., R. Hagen, and M. Knuth, "Method for Obtaining Aromatics and Dyestuffs from Bell Peppers," U.S. Patent 4,400,398 (1983).

79. Schutz, E., K. R. Vollbrecht, K. Sander, T. Sand, and P. Muhlnickel, "Method of Extracting the Flavoring Substances from the Vanilla Capsule," U.S. Patent 4,470,927 (1984).

80. Anon., "Diets: No Yoke!," Newsweek July 14, 5 (1986).

81. Zosel, K., "Process for Recovering Caffeine," U.S. Patent 3,806,619 (1974).

82. Laws, D. J. R., N. A. Bath, C. S. Ennis, and A. G. Wheldon, "Hop Extraction with Carbon Dioxide," U.S. Patent 4,218,491 (1980).

83. Stahl, E., "Coupling of Extraction with Supercritical Gases and Thin-Layer Chromatography," J. Chrom. 142, 15-21 (1977).

84. Sugiyama, K., and M. Saito, "Simple Microscale Supercritical Fluid Extraction System and its Application to Gas Chromatography-Mass Spectrometry of Lemon Peel Oil," J. Chrom. 442, 121-131 (1988).

85. deFilippi, R. P., and M. E. Chung, "Laboratory Evaluation of Critical Fluid Extractions for Environmental Applications," EPA Report 600/2-85-045, April (1985).

86. Raymer, J. H., and E. D. Pellizzari, "Toxic Organic Compound Recoveries from 2,6-Diphenyl-p-phenylene Oxide Porous Polymer Using Supercritical Carbon Dioxide and Thermal Desorption Methods," Anal. Chem. 59, 1043-1048 (1987).

87. Van Alsten, J. G., P. C. Hansen, and C. A. Eckert, "Supercritical Enhancement Factors for Nonpolar and Polar Systems," Paper 84a presented at the AIChE Annual Meeting, San Francisco, CA (1984).

88. Bamberger, T., J. C. Erickson, C. L. Charles, and S. K. Kumar, "Measurement and Model Prediction of Solubilities of Pure Fatty Acids, Pure Triglycerides, and Mixtures of Triglycerides in Supercritical Carbon Dioxide," J. Chem. Eng. Data 33, 327-333 (1988).

89. Kurnik, R. T., S. J. Holla, and R. C. Reid, "Solubility of Solids in Supercritical Carbon Dioxide and Ethylene," J. Chem. Eng. Data 26, 47-51 (1981).

90. Johnston, K. P., D. H., Ziger, and C. A. Eckert, "Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented Van der Waals Treatment," Ind. Eng. Chem. Fundam. 21, 191-197 (1982).

91. Johnston, K. P., and C. A. Eckert, "An Analytical Carnahan-Starling-van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids," AICHE Journal 27, 773-779 (1981).

92. Mackay, M. E., and M. E. Paulaitis, "Solid Solubilities of Heavy Hydrocarbons in Supercritical Solvents," Ind. Eng. Chem. Fundam. 18, 149-153 (1979).

93. Peng, D.-Y., and D. B. Robinson, "A New Two-Constant Equation of State," Ind. Eng. Chem. Fundam. 15, 59-64 (1976).

94. Engelhardt, H., and A. Gross, "On-Line Extraction and Separation by Supercritical Fluid Chromatography with Packed Columns," J. High Resol. Chrom. & Chrom. Communic. 11, 38-42 (1988).

95. Brunner, G., "Selectivity of Supercritical Compounds and Entrainers with Respect to Model Substances," Fluid Phase Equilibria 10, 289-298 (1983).

96. Stahl, E., and K. W. Quirin, "Dense Gas Extraction on a Laboratory Scale: A Survey of Some Recent Results," Fluid Phase Equilibria 10, 269-278 (1983).

97. William, D. F., "Review Article Number 5 -- Extraction with Supercritical Gases," Chem. Eng. Sci. 36, 1789-1781 (1981).

98. Saito, M., Y. Yamauchi, H. Kashiwazaki, and M. Sugawara, "New Pressure Regulating System for Constant Mass-Flow Supercritical Fluid Chromatography and Physico-Chemical Analysis of Mass-Flow Reduction in Pressure Programming by Analogous Circuit Model," Chromatographia 25, 801-805 (1988).

99. Pariente, G. L., S. L. Petoney, Jr., P. R. Griffith, and K. H. Shafer, "Computer-Controlled Pneumatic Amplifier Pump for Supercritical Fluid Chromatography and Extractions," Anal. Chem. 59, 808-813 (1987).

100. Sunol, A. K., B. Hagh, and S. Chen, "Entrainer Selection in Supercritical Extraction," in Supercritical Fluid Technology, edited by J. M. L. Penninger, J. Radosz, M. A. McHugh, and V. J. Krukonis; Elsevier, 451-464 (1985).

101. Hoyer, G. G., "Extraction with Supercritical Fluids: Why, How, and So What," Chemtech 440-448 (1985).

102. Mitra, S., J. W. Chem, and D. S. Viswanath, "Solubility and Partial Molar Volumes of Heavy Aromatic Hydrocarbons in Supercritical CO_2," J. Chem. Eng. Data 33, 35-37 (1988).

103. Vezzeti, D. J., "Solubility of Solids in Supercritical Gases," J. Chem. Phys. 77, 1512-1516 (1982).

104. Vezzeti, D. J., "Solubility of Solids in Supercritical Gases II Extension to Molecules of Differing Sizes," J. Chem. Phys. 77, 1512-1516 (1982).

105. Chrastill, J., "Solubility of Solids in Supercritical Gases," J. Phys. Chem. 86, 3016-3021 (1982).

106. Schnitzer, M., and C. M. Preston, "Supercritical Gas Extraction of a Soil with Solvents of Increasing Polarities," Soil Sci. Soc. Am. J. 51, 639-649 (1987).

107. Joshi, D. K., and J. M. Prausnitz, "Supercritical Fluid Extraction with Mixed Solvents," AIChE Journal 30, 522-525 (1984).

108. Kim, S., and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," AIChE Journal 33, 1602-1611 (1987).

109. Larson, K. S., and M. L. King, "Evaluation of Supercritical Fluid Extraction in the Pharmaceutical Industry," Biotechnology Progress 2, 73-82 (1986).

110. Ikushima, Y., T. Goto, and M Arai, "Modified Solubility Parameter as an Index to Correlate Solubility in Supercritical Fluids," Bull. Chem. Soc. Jpn. 60, 4145-4147 (1987).

111. Schmitt, W. J., and R. C. Reid, "The Solubility of Paraffinic Hydrocarbons and Their Derivation in Supercritical Carbon Dioxide," Chem. Eng. Comm. 64, 155-176 (1988).

112. Smith, R. D., H. R. Udseth, B. W. Wright, and C. R. Yonker, "Solubilities in Supercritical Fluids: The Application of Chromatographic Measurement Methods," Separation Sci. Technol. 22, 1065-1086 (1987).

113. Allada, S. R., "Solubility Parameters of Supercritical Fluids," Ind. Eng. Chem. Process Res. Dev. 23, 344-348 (1984).

114. Scholsky, K. M., "Process Polymers with Supercritical Fluids," Chemtech 750-757 (1987).

115. Lee Scientific, Inc., "Supercritical Fluid Chromatographic Methods for Nonvolatile Organic Compounds," Final Report for EPA Contract 69-4435 (1988).

116. King, J. W., "Supercritical Fluid-Based Techniques for Pesticide Extraction and Analysis," paper presented at the 196th ACS National Meeting, Division of Agrochemicals, Los Angeles, California (1988).

117. Lamarche, P., S. A., McClintock, and M. Dimaso, "A Technique for the Modification of Supercritical Fluid Mobile Phases," LC.GC Magazine 6(2), 154-155 (1989).

118. Raynie, D. F., S. M. Fields, N. M. Djordevic, K. E. Markides, and M. L. Lee, "A Method for the Preparation of Binary Mobile Phase Mixtures for Capillary Supercritical Fluid Chromatography," J. High Resol. Chrom. 12, 51-52 (1989).

119. Nielen, M. W. F., J. T. Sanderson, R. W. Frei, and U. A. Th. Brinkman, "On-Line System for Supercritical Fluid Extraction and Capillary Gas Chromatography With Electron-Capture Detection," J. Chrom. 474, 388-395 (1989).

120. Janda, V., G. Steenbeke, and P. Sandra, "Supercritical Fluid Extraction of s-Triazine Herbicides From Sediment," J. Chrom. 479, 200-205 (1989).

121. Onuska, F. E., and K. A. Terry, "Supercritical Fluid Extraction of PCBs in Tandem With High Resolution Gas Chromatography in Environmental Analysis," J. High Resol. Chrom. 12, 527-531 (1989).

122. Onuska, F. E., and K. A. Terry, "Supercritical Fluid Extraction of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Sediment Samples," J. High Resol Chrom. 12, 357-361 (1989).

123. Phillips, J. H., and R. J. Robey, "Solvent Strength and Selectivity Properties of Supercritical Carbon Dioxide Relative to Liquid Hexane," J. Chrom. 465, 177-188 (1989).

124. Hawthorne, S. B., M. S. Krieger, and D. J. Miller, "Supercritical Carbon Dioxide Extraction of Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons, Heteroatom-Containing Polycyclic Aromatic Hydrocarbons, and n-Alkanes From Polyurethane Foam Sorbents," Anal. Chem. 61, 736-740 (1989).

125. Alexandrou, N., and J. Pawlizyn, "Supercritical Fluid Extraction for the Rapid Determination of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Municipal Incinerator Fly Ash," Anal. Chem. 61, 2770-2776 (1989).

126. Saito, M., Y. Yamauchi, K. Inomata, and W. Kottkamp, "Enrichment of Tocopherols in Wheat Germ by Directly Coupled Supercritical Fluid Extraction With Semipreparative Supercritical Fluid Chromatography," J. Chrom. Sci. 27, 79-85 (1989).

127. Hawthorne, S. B., D. J. Miller, and J. J. Langenfeld, "Quantitative Analysis Using Directly Coupled Supercritical Fluid Extraction-Capillary Gas Chromatography (SFE-GC) With a Conventional Split/Splitless Injection Port," J. Chrom. Sci. 28, 2-8 (1990).

128. Hawthorne, S. B., D. J. Miller, and M. S. Krieger, "Coupled SFE-GC: A Rapid and Simple Technique for Extracting, Identifying, and Quantitating Organic Analytes From Solids and Sorbent Resins," J. Chrom. Sci. 27, 347-354 (1989).

129. King, J. W., "Fundamentals and Applications of Supercritical Fluid Extraction in Chromatographic Science," J. Chrom. Sci. 27, 355-364, (1989).

130. King, J. W., "Applications of Capillary Supercritical Fluid Chromatography-Supercritical Fluid Extraction to Natural Products," J. Chrom. Sci. 28, 9-14 (1990).

131. Levy, J. M., R. A. Cavalier, T. N. Bosch, A. F. Rynaski, and W. E. Huhak, "Multidimensional Supercritical Fluid Chromatography and Supercritical Fluid Extraction," J. Chrom. Sci. 27, 341-346 (1989).

132. Andersen, M. R., J. T. Swanson, N. L. Porter, and B. E. Richter, "Supercritical Fluid Extraction as a Sample Introduction Method for Chromatography," J. Chrom. Sci. 27, 371-377 (1989).

133. Xie, Q. L., K. E. Markides, and M. L. Lee, "Supercritical Fluid Extraction-Supercritical Fluid Chromatography With Fraction Collection For Sensitive Analytes," J. Chrom. Sci. 27, 365-370 (1989).

134. Liebman, S. A., E. J. Levy, S. Lurcott, S. O'Neill, J. Guthrie, T. Ryan, and S. Yocklovich, "Integrated Intelligent Instruments: Supercritical Fluid Extraction, Desorption, Reaction, and Chromatography," J. Chrom. Sci. 27, 118-126 (1989).

APPENDIX B

EXTRACTION PROCEDURE USING SUPERCRITICAL FLUIDS

7-3

EXTRACTION PROCEDURE USING SUPERCRITICAL FLUIDS

1.0 SCOPE AND APPLICATION

1.1 This method describes the extraction of organic compounds from soils, sediments, fly ash, and other solid materials using supercritical fluids. The method is suitable for use with any supercritical fluid extraction system that allows extraction conditions (e.g., pressure, temperature, flowrate, modifiers) to be adjusted to achieve separation of the target analytes from the matrices.

1.2 The method is applicable to the extraction of organochlorine pesticides, polychlorinated biphenyls (PCBs), nitroaromatics, haloethers, polynuclear aromatic hydrocarbons, organophosphorus pesticides, and other compounds on the EPA's Priority Pollutant List.[1]

2.0 SUMMARY OF METHOD

2.1 A known amount of sample is transferred to the extraction vessel. The sample is then extracted for up to 60 min with supercritical carbon dioxide (other compounds have been used or proposed as supercritical fluids), with or without modifier, at pressures of 150 to 350 atm and temperatures of 50 to 70°C, as detailed below. Supercritical pressures are maintained inside the extraction vessel by using a 50-μm ID x 60-cm length uncoated fused-silica capillary as restrictor. The extracted organics are collected in an organic solvent (5 mL) upon depressurization of the carbon dioxide. The extract is then analyzed as is or it is further concentrated to 1 mL and/or subjected to cleanup prior to analysis.

2.2 Safety considerations:

2.2.1 A safety feature such as over-pressure limit is required on the extractor. This feature should be designed to protect the pump, the downstream components, and the laboratory personnel from possible damage or injuries resulting from equipment failure under high pressures.

2.2.2 Fittings used for the extraction vessel must be capable of withstanding the required extraction pressures. The maximum operating pressure for the Suprex Corporation Model SE-50 extractor is 500 atm. When other systems are used, check with the manufacturer of the particular system to find out what the maximum operating pressure is for that system. Make sure that the extraction vessels are rated for such pressures.

2.2.3 Nitrous oxide, which has also been used as supercritical fluid, is a strong oxidant and may cause an explosion when large amounts of easily oxidized materials come in contact with nitrous oxide at elevated temperatures.

---

[1] To generate the data in this protocol, a Suprex Model SE-50 extractor was used. Other instruments may be used in place of the Suprex extractor.

2.2.4 Combining modifiers with supercritical fluids requires an understanding and evaluation of the potential chemical interaction of the modifier and the supercritical fluid, as well as interactions of the supercritical fluid or modifier with the analyte(s) or the matrix. Table 1 is a summary of supercritical fluids with modifiers which are offered by Scott Specialty Gases.

3.0 INTERFERENCES

3.1 Supercritical fluids must be demonstrated to be free from interferences by the analysis of system blanks. Purification by passing the fluid through a special trap may be required. Refer to Section 4.4 of this method for specific guidance.

3.2 The extraction vessel(s), the frits, the restrictor, and the selector valve may retain solutes whenever high-concentration samples are extracted. It is, therefore, good practice to replace or clean the extraction vessel after each extraction. Replacement of the restrictor may be necessary when system blanks indicate carryover. At least one system blank should be performed daily while the instrument is in use. Furthermore, system blanks should be performed after each extraction of a high-concentration sample (concentration in the ppm range). If system blanks continue to indicate contamination even after replacement of the extraction vessel and the restrictor, the 4-port valve must be cleaned.

4.0 APPARATUS AND MATERIALS

4.1 Syringe pump and associated hardware -- Syringe pump module capable of withstanding high pressure (500 atm) and with a capacity of up to 250 mL. A schematic diagram of a syringe pump module is given in Figure 1. The pump consists of a high-pressure cylinder and a piston. The piston is drived by a stepper motor. The motion rate of the piston must be controlled very accurately to generate the desired pressure/density, or flowrate.

As shown in Figure 1, the fluid flows from the tank through a stainless steel line to the bulkhead fitting on the rear of the pump module. From this bulkhead fitting, fluid flows through 1/8-in stainless-steel tubing to the inlet valve, which is a manual on/off valve, and into the syringe pump. From the discharge of the syringe pump, the fluid flows to a tubing cross that connects to the pressure transducer and to the safety-head assembly (i.e., rupture disk). The rupture disk outlet must be piped to a vent system. From the cross, the fluid flows to a manual on/off outlet valve.

Behind the outlet valve, the 1/8-in tubing is reduced to 1/16 in and connected to a 2-μm cup filter. The outlet filter is located on the inside of the pump housing. Past the filter, the mobile phase flows through 1/16-in tubing that runs through the control module to the oven module. At the oven module, the tubing is connected to the vent/purge valve and then to the extraction vessel.

226

4.1.1 Solvent modifier valve (optional) -- Suprex Corporation offers a valve (catalog no. 201-103) which, when installed in the fluid inlet line, allows the user to accurately and reproducibly add modifiers to the extraction fluid. Follow manufacturer's instructions for installation, operation, changing modifiers, valve disassembly, cleaning, and assembly. The solvent modifier valve is not needed when commercially available mixtures of carbon dioxide and modifiers are used. Systems from other manufacturers may offer similar devices.

4.1.2 Other types of pumps can be used to effectively deliver supercritical carbon dioxide or other fluids to the extractor, including piston pumps and diaphragm pumps.

4.2 Control module -- This module controls the functions of the pump and the oven modules and provides the user interface to the microprocessor control system. Follow manufacturer's instructions for using this device.

4.3 Oven -- The oven module comprises the vent/purge valve, the extraction vessel, the 4-port valve, the restrictor, and the collection vial (Figure 2). The vent/purge valve is mounted on top of the oven, and the extraction vessel and the two multiport valves are mounted inside the oven. The restrictor(s) run from inside the oven to the collection vial(s) which are located outside the oven.

4.3.1 Extraction vessel -- 7.85-mL volume (1 cm ID x 10 cm length) or 4.7-mL volume (1 cm ID x 6 cm length), stainless-steel vessel with end fittings and 2-µm frits. Other extraction vessel sizes (usually smaller) are also available.

4.3.2 4-Port valve (electronically actuated), Suprex Corporation, catalog no. 100-011, or equivalent.

4.3.3 Valco rotor for 4-port valve, Valco Instruments, catalog no. SSA-CSD4UWT, or equivalent.

4.3.4 Restrictor -- 50-µm ID x 375-µm OD x 60-cm length piece of uncoated fused-silica tubing (J&W Scientific or equivalent). Other restrictors may be used including tapered restrictors, static pinhole restrictors, frit restrictors, and variable orifice restrictors (manual- and computer-controlled). Check with the manufacturer of the supercritical fluid extraction system on the advantages of various restrictor designs.

4.3.5 Collection vial -- 10-mL capacity with screw cap; in order to accommodate the restrictor, the cap should have a 3-mm hole.

4.4 Carbon dioxide cleanup system (optional) -- White Associates, catalog nos. 400 and 401, provides a fluid cleanup system that allows the use of a less-expensive grade of carbon dioxide, e.g., Coleman grade, instead of the SFC grade, or it can be used to further improve the quality of the

SFC-grade carbon dioxide. The system removes hydrocarbons, water, and other impurities commonly found in bottled carbon dioxide. The adsorbent contained in the trap will last for one tank of Coleman grade or four tanks of SFC-grade carbon dioxide.

4.5 Carbon dioxide cylinder balance (optional) -- White Associates, catalog no. 30, or Scott Specialty Gases Model 5588D, or equivalent, balances can be used to track the fluid usage. Such a device is useful because carbon dioxide tanks used for SFE are not equipped with regulators, and it is difficult to determine when the tank needs to be replaced. The White Associates scale comes with a ramp and has a capacity of 250 lbs; the weight is determined in 1-lb increments.

4.6 Tools required include: screwdriver (flat-blade), adjustable wrench, pliers, tubing cutter, and various small open-end wrenches for small fittings.

5.0 REAGENTS

5.1 Carbon dioxide -- This fluid is available in SFC or SFE grade from Scott Specialty Gases Inc., Liquid Carbonic Specialty Gas Corporation, and Matheson Gas Products. When other grades are considered, the fluid must be purified prior to use, e.g., by using the procedure described in Section 4.4. Aluminum cylinders are preferred over steel cylinders. The cylinders are fitted with eductor tubes, and their contents are under 1500 psi of helium head pressure.

5.2 Carbon dioxide with modifiers -- mixtures are available from Scott Specialty Gases (Table 1).

5.3 Surrogate standard spiking solution.

5.3.1 The surrogate standard is added to all samples, blanks, matrix spike, matrix spike duplicates; the compounds specified for this purpose are nitrobenzene-d_5, 2-fluorophenol, 2,4,6-tribromophenol, 2-fluorobiphenyl, and phenol-d_5. These compounds can be used only when the extracts are analyzed by GC/MS. Other compounds listed in the SW-846 methods can be used. The only requirements for surrogates are that they need to be spiked in a solvent that is compatible with the fluid used for extraction and that the volume of solvent added does not exceed 300 µL.

5.3.2 Make a composite solution of the surrogate compounds at 1,000 ng/mL in methanol, and spike 300 µL of this solution to each sample after the sample has been placed in the extraction vessel.

5.3.3 At least one surrogate compound should be spiked into the solvent in the collection vessel to determine the collection efficiency. Terphenyl-d_{14} is recommended for this purpose if the extract will be analyzed by GC/MS. Prepare a solution at 5,000 ng/mL in methanol. Spike 20 µL of this solution into each collection vessel containing the appropriate solvent.

5.4 Solvents -- Hexane, methylene chloride, methanol (pesticide-quality or equivalent). Hexane is used as the collection solvent whenever carbon dioxide is used for extraction, and methylene chloride is recommended for use as collection solvent whenever carbon dioxide containing methanol is used for extraction. Methanol is used to prepare the surrogate spiking solution and as modifier. Other solvents can be used if the user demonstrates that they are applicable to a particular situation.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Follow instructions in the SW-846 protocol, Section 4.1.

7.0 PROCEDURE

7.1 Sample preparation

7.1.1 Sediment/soil samples -- Decant and discard any excess water. Mix thoroughly, especially samples that have been composited. Discard any foreign objects such as sticks, leaves, and rocks. Air-drying of the sample is not recommended.

7.1.2 Waste samples -- Multiphase samples must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding -- Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of moisture content -- When the analytical results are reported on a dry-weight basis, a portion of the sample should be weighed out for moisture determination, at the same time that the portion used for the analytical determination is weighed out.

7.2.1 Immediately after weighing the sample for extraction, weigh 5 to 10 g of the sample into a tared precleaned aluminum dish. Determine the moisture content by drying overnight at 105°C. Allow to cool in a desiccator before weighing.

$$\%\ \text{moisture} = 100 \times \frac{(\text{g of sample} - \text{g of dry sample})}{\text{g of sample}}$$

7.3 Sample extraction

7.3.1 Weigh the specified amount of sample in a precleaned aluminum dish.

7.3.2 Transfer the weighed sample to a clean extraction vessel making sure that none of the sample is lost. Spike with the surrogates.

Use two plugs of silanized glass wool to hold the sample in place. Attach the end fittings and install the extraction vessel in the oven.

7.3.3 Fill the collection vessel with 5 mL hexane or methylene chloride and spike it with the surrogate compound that is used to determine the collection efficiency. The selection of this surrogate compound depends on what method will be used to analyze the extract. Terphenyl-d_{14} is recommended for those samples that will be analyzed by GC/MS using Method 8270. Refer to other applicable SW-846 methods for the use of other compounds.

7.3.4 Set the pressure, temperature, position of the 4-port valve, etc. Tables 2 through 7 give specific conditions for 41 organochlorine pesticides, 47 organophosphorus pesticides, 36 nitroaromatics, 19 haloethers, 43 base/neutral/acidic compounds, and 16 polynuclear aromatic hydrocarbons. Follow the manufacturer's instructions in setting up the instrument using the recommended conditions.

7.3.5 Before filling the pump with carbon dioxide, verify that all fittings for the fluid supply tubing are tightened properly and that the outlet valve is closed. Press the FILL key on the keyboard and allow the pump pressure to decrease below the cylinder pressure. This value is dependent upon the helium head pressure in the cylinder and the room temperature. To be safe, depressurize to 70 atm. Open the valve on the cylinder by rotating it counterclockwise. Open the inlet valve on the pump to allow carbon dioxide to enter the pump. When the fill cycle has been completed, the pump is filled with carbon dioxide and the pump piston stops. Open the outlet valve and the vent/purge valve to ensure that liquid is flowing through the system. Close the vent/purge valve, then the outlet valve. Close the pump inlet valve and then close the supply cylinder valve.

7.3.6 Equilibrate the system to the desired parameters by pressing the EQUIL key. Make sure the vent/purge valve is closed and the outlet valve on the syringe pump is open. The system pressure will return to the value set in the active method. When the system is ready, press the RUN key.

7.3.7 After the run time has elapsed, the system will automatically go to the equilibrate mode. At this point, remove the collection vessel(s) containing the extract. More than one extract may be collected from one sample, depending on method specifications. Since the depressurization of the carbon dioxide at the end of the restrictor outlet results in a gas flow rate of about 120 mL/min, part of the collection solvent will evaporate during the extraction. However, cooling caused by the rapid expansion of the carbon dioxide reduces the loss of solvent so that approximately 3 mL remain after a 30-min extraction. The extract is then reconstituted to the original 5 mL volume or concentrated further.

7.3.8 Depressurize the system by closing the outlet valve and opening the vent/purge valve. When the system is depressurized, the extraction vessel can be removed and cleaned and the system can be set up for the next extraction. Make sure that the outlet valve on the pump is closed before depressurizing the system.

7.4 The procedure to be followed in emptying the syringe pump depends upon the type of fluid being used. In the case of carbon dioxide, nitrous oxide, and ammonia, which are gases at ambient temperature and pressure, it is only necessary to vent the gas to a fume hood by allowing it to expand across the purge valve. If solvents such as methanol, pentane, or diethyl ether are used in the pump, the solvent is collected in a suitable collection vessel.

7.4.1 Stop the pump operation by pressing the STOP key.

7.4.2 Attach either a 1/16-in tube to the exit from the vent/purge valve (for purging gases) or put a collection vessel in place (for collecting liquids).

7.4.3 Open the vent/purge valve slowly by rotating it counterclockwise until completely open. Rotate it a half turn to prevent valve wear.

7.4.4 Press the EMPTY key. The piston will be driven at its maximum rate until the pump is empty. When the pump cycle has been completed, the PUMP EMPTY indicator will appear on the screen.

7.5 To change fluids, it is necessary to empty the syringe pump as described in Section 7.4. Upon completion of the emptying procedure, the piston will be at its maximum extension and the pump outlet valve and purge valve will be open. Proceed as follows:

7.5.1 Connect the new fluid supply cylinder to the syringe pump inlet line and open the supply cylinder valve.

7.5.2 Open the pump inlet valve. The new fluid will flow through the inlet line to the pump and out through the vent. This operation should be continued for a few minutes to purge out any remaining old fluid.

7.5.3 Close the pump outlet valve and the vent/purge valve.

7.6 Restrictor removal and installation

7.6.1 The fused-silica restrictor connects to the 4-port valve with a 1/16 to 1/32-in reducer. The restrictor is attached to the reducer by threading one end through the 1/32-in gland, the FS.4 vespel ferrule, and the 1/16-in fitting. Push the restrictor through the reducer about 5 cm and cut off about 3 cm. Pull the restrictor back through the reducer tip until the end of the restrictor is about 0.4 mm inside the tip of the reducer fitting. Tighten the 1/32-in reducer gland. Attach the restrictor with the reducer to any of the four 1/16-in fittings.

7.6.2 Remove the restrictor by loosening the 1/32-in gland and pull the restrictor out of the reducer. The FS.4 ferrule remains lodged inside the reducer and can be reused if the outside diameter of the new restrictor is equal or less than the one just removed. If the FS.4 ferrule cannot be rethreaded, the reducer can be heated with a propane torch to remove the ferrule.

8.0 QUALITY CONTROL

8.1 Reagent blanks or matrix-spiked samples must be subjected to the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific Quality Control procedures and to Method 3500 for sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data. Tables 2 through 7 give recovery data for 41 organochlorine pesticides, 47 organophosphorus pesticides, 36 nitroaromatics, 19 haloethers, 43 base/neutral/acidic compounds, and 16 polynuclear aromatic hydrocarbons, and the conditions under which these data were obtained.

TABLE 1. SUMMARY OF SF MIXTURES[a]

SF	Carbon dioxi	Sulfur hexafluoride	Freon 13
Modifier	Methanol	Ammonia	N-propylamine
	Ethanol	Sulfur dioxide	
	Propanol		
	Hexanol		
	Tetrahydrofuran		
	Acetonitrile		
	Chloroform		
	Methylene chloride		
	Methyl chloride		
	Dioxane		
	2-Methoxyethanol		
	Dimethylsulfoxide		
	Acetic acid		
	Formic acid		
	N,N-dimethylacetamide		
	Sulfur hexafluoride		
	Trichlorofluoromethane		
	Carbon disulfide		
	Sulfur dioxide		
	Propylene carbonate		

[a] These mixtures are available from Scott Specialty Gases. At the time this version of the SFE protocol was written, only very limited experience with supercritical carbon dioxide with modifiers other than methanol was available.

TABLE 2. PERCENT RECOVERIES OF 41 ORGANOCHLORINE PESTICIDES FROM SPIKED SAND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE WITH 10 PERCENT METHANOL[a]

Compound no.	Compound	Spike level (ng/g)	Average Recovery	Percent RSD
1	alpha-BHC	62.5	93.6	16.8
2	gamma-BHC	62.5	121	10.8
3	beta-BHC	62.5	93.6	25.2
4	Heptachlor	62.5	91.7	23.0
5	delta-BHC	62.5	103	19.9
6	Aldrin	62.5	98.7	15.9
7	Heptachlor epoxide	62.5	88.6	12.2
8	Endosulfan I	62.5	88.2	10.3
9	4,4'-DDE	62.5	95.4	10.6
10	Dieldrin	62.5	103	19.6
11	Endrin	62.5	92.8	13.6
12	4,4'-DDD	125	120	10.1
13	Endosulfan II	62.5	89.6	6.9
14	4,4'-DDT	62.5	99.9	4.9
15	Endrin aldehyde	125	120	10.8
16	Endosulfan sulfate	62.5	125	8.8
17	Methoxychlor	62.5	107	2.4
18	Endrin ketone	62.5	98.1	6.7
19	Hexachlorocyclopentadiene	62.5	26.1	13.7
20	Etridiazole	62.5	87.9	14.5
21	Chloroneb	1,250	92.5	20.8
22	Propachlor	1,250	95.8	22.1
23	Hexachlorobenzene	62.5	114	7.3
24	Trifluralin	125	94.5	19.7
25	Diallate	1,875	109	9.9
26	Pentachloronitrobenzene	62.5	97.8	14.8
27	Chlorothalonil	125	93.4	9.9
28	Alachlor	625	103	20.5
29	DCPA	62.5	107	5.9
30	Isodrin	62.5	98.6	17.9
31	trans-Permethrin	625	102	17.9
32	gamma-Chlordane	62.5	95.8	18.5
33	alpha-Chlordane	62.5	99.8	11.4
34	trans-Nonachlor	62.5	108	11.4
35	Captan	125	95.0	6.5
36	Perthane	1,875	79.0	8.9
37	Chlorobenzilate	125	28.4	12.6
38	Chloropropylate	62.5	109	10.3
39	Kepone	62.5	106	19.5
40	Mirex	125	96.4	3.7
41	DBCP	62.5	35.4	29.2

[a] The extraction was performed at 150 atm/50°C (10 min static) followed by 200 atm/60°C (10 min dynamic) and 250 atm/70°C (10 min dynamic). The number of determinations was 3. The sample size was 8 g.

TABLE 3. PERCENT RECOVERIES OF 47 ORGANOPHOSPHORUS PESTICIDES FROM SPIKED SAND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE WITH 10 PERCENT METHANOL[a]

Compound no.	Compound	Exp. 1	Exp. 2	Exp. 3
1	Dichlorvos	97.6	96.7	95.5
2	Mevinphos	97.8	99.7	102
3	Ethoprop	83.5	82.3	91.4
4	Naled	22.9	14.5	4.8
5	Sulfotep	70.1	71.0	66.5
6	Phorate	0	0	0
7	Dimethoate	72.0	76.7	79.3
8	Diazinon	0	0	0
9	Disulfoton	78.2	77.7	73.9
10	Parathion methyl	89.1	90.9	98.0
11	Ronnel	94.0	97.7	92.8
12	Malathion	76.3	77.0	78.3
13	Fenthion	82.4	82.4	80.6
14	Chlorpyrifos	72.7	70.0	69.4
15	Parathion ethyl	86.8	87.6	91.8
16	Stirophos	87.1	116	92.3
17	Fensulfothion	82.9	117	93.8
18	Bolstar	78.2	105	80.8
19	EPN	83.3	83.9	88.7
20	Azinphos methyl	75.9	79.4	84.0
21	Coumaphos	77.3	78.7	81.7
22	Demeton-S	0	0	0
23	Demeton-O	0	0	0
24	Merphos	87.5	--	105
25	Ethion	78.4	80.7	82.0
26	Trimethyl phosphate	124	110	135
27	Hexamethyl phosphoramide	92.6	111	107
28	Trichlorfon	24.1	17.1	23.1
29	TEPP	6.0	9.9	5.0
30	Thionazin	84.5	74.9	84.0
31	Monocrotophos	54.9	59.4	70.6
32	Terbufos	80.5	81.0	81.1
33	Tricresyl phosphate	80.5	81.0	81.1
34	Fonophos	75.3	72.1	67.8
35	Dichlorphenthion	91.6	92.9	93.7
36	Phosphamidon	91.6	92.9	93.7
37	Methyl chlorpyrifos	79.6	77.2	73.2
38	Fenithrothion	85.7	92.1	83.8
39	Aspon	82.0	82.1	81.8
40	Trichloronate	82.0	82.1	81.8
41	Chlorfevinphos	81.6	101	83.4
42	Crotoxyphos	67.9	68.3	91.9
43	Tokuthion	79.7	78.9	78.4
44	Famphur	83.5	93.2	98.6
45	Phosmet	64.6	20.6	57.7
46	Leptophos	84.8	87.9	90.8
47	Azinphos ethyl	76.0	82.7	87.0

[a] The extraction conditions were as follows: Exp. 1 -- 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/10 min dynamic; Exp. 2 -- 200 atm/60°C/30 min dynamic; Exp. 3 -- 250 atm/70°C/30 min dynamic. Single determination. The sample size was 8 g. The spiking level was 2.5 µg/g per compound.

TABLE 4. PERCENT RECOVERIES OF 36 NITROAROMATICS FROM SPIKED SAND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Fraction 1		Fraction 2		Fraction 1	
		Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 3	Exp. 4
1	Nitrobenzene	44.5	42.4	0	0	0	0
2	o-Nitrotoluene	67.9	64.3	0	0	0	0
3	m-Nitrotoluene	62.2	59.1	0	0	29.7	25.8
4	p-Nitrotoluene	65.9	62.2	0	0	50.5	42.5
5	1-Chloro-3-nitrobenzene	63.0	61.5	0	0	18.1	15.7
6	1-Chloro-4-nitrobenzene	64.9	64.0	0	0	26.1	23.3
7	1-Chloro-2-nitrobenzene	67.5	67.2	0	0	24.1	21.3
8	2-Chloro-6-nitrotoluene	67.6	66.5	0	0	27.6	24.5
9	4-Chloro-2-nitrotoluene	69.5	68.5	0	0	37.3	33.6
10	3,5-Dichloronitrobenzene	66.3	66.7	0	0	40.7	37.0
11	2,5-Dichloronitrobenzene	71.7	71.5	0	0	40.1	36.1
12	2,4-Dichloronitrobenzene	75.6	75.8	0	0	53.6	48.8
13	4-Chloro-3-nitrotoluene	79.5	76.4	0	0	58.4	53.9
14	3,4-Dichloronitrobenzene	76.3	77.0	0	0	59.1	53.6
15	2,3-Dichloronitrobenzene	78.1	78.5	0	0	58.9	53.6
16	2,4,6-Trichloronitrobenzene	66.8	66.4	0	0	55.7	51.3
17	1,4-Naphthoquinone	74.6	76.3	0	0	42.8	38.5
18	1,2,4-Trichloro-5-nitrobenzene	78.8	79.6	0	0	71.4	65.5
19	1,4-Dinitrobenzene	62.1	62.2	0	0	61.7	58.2
20	2,6-Dinitrotoluene	77.8	79.5	1.8	0	79.6	73.5
21	1,3-Dinitrobenzene	66.6	68.5	0	0	68.0	63.3
22	1,2,3-Trichloro-4-nitrobenzene	80.2	80.7	0	0	75.8	69.8
23	2,3,5,6-Tetrachloronitrobenzene	78.2	80.3	0	0	68.4	62.7
24	1,2-Dinitrobenzene	67.6	69.7	0	0	63.0	58.9
25	2,4-Dinitrotoluene	68.3	68.4	0	0	59.6	58.0
26	1-Chloro-2,4-dinitrobenzene	78.7	79.3	0	0	79.0	73.5
27	2,3,4,5-Tetrachloronitrobenzene	83.2	84.0	0	0	84.4	77.9
28	1-Chloro-3,4-dinitrobenzene	75.7	76.1	0	0	76.9	71.0
29	Trifluralin	85.2	86.5	0	0	86.2	79.2
30	Benefin	85.4	86.5	0	0	89.5	81.7
31	Pentachloronitrobenzene	82.7	84.8	0	0	82.0	76.0
32	Profluralin	90.7	90.5	0	0	90.2	83.5
33	Dinitramine	84.1	85.1	0	0	87.3	80.9
34	Butralin	85.9	86.4	0	0	91.1	83.1
35	Isopropalin	86.6	85.8	0	0	89.5	82.7
36	Penoxalin	70.1	71.3	5.4	0	72.3	70.1

[a] Experiments 1 and 2 are identical samples (2.5 g sand) extracted in parallel at 150 atm (50°C) 10 min dynamic followed by 200 atm/60°C/10 min dynamic and 250 atm/70°C/30 min dynamic for Fraction 1 and 300 atm/70°C/30 min dynamic for Fraction 2. Experiments 3 and 4 were also identical samples (2.5 g sand) extracted in parallel at 300 atm/70°C/60 min dynamic. The spiking level was 600 ng/g per compound.

TABLE 5. PERCENT RECOVERIES OF 19 HALOETHERS FROM SPIKED SAND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE

Compound no.	Compound	Exp. 1[a]	Exp. 2[a]	Exp. 3[b]	Exp. 4[b]	Exp. 5[c]	Exp. 6[c]	Exp. 7[d]	Exp. 8[d]
1	4-Bromophenyl-phenyl ether	95.3	84.2	63.5	58.0	90.3	99.7	70.8	78.1
2	Phenyl-4'-nitrophenyl ether	88.5	78.0	55.2	59.8	72.6	91.0	69.2	78.6
3	2-Chlorophenyl-4'-nitrophenyl ether	89.5	78.2	62.3	68.1	77.1	89.1	70.4	75.9
4	3-Chlorophenyl-4'-nitrophenyl ether	86.7	75.3	55.8	61.1	71.0	85.0	69.7	76.6
5	4-Chlorophenyl-4'-nitrophenyl ether	89.5	78.4	46.3	56.1	66.5	89.3	60.8	74.3
6	2,6-Dichlorophenyl-4'-nitrophenyl ether	88.2	76.3	60.8	66.5	76.5	89.2	70.0	75.6
7	3,5-Dichlorophenyl-4'-nitrophenyl ether	87.1	75.8	60.6	61.0	69.5	82.9	74.0	78.3
8	2,5-Dichlorophenyl-4'-nitrophenyl ether	87.1	75.8	60.6	61.0	69.5	82.9	74.0	78.3
9	2,4-Dichlorophenyl-4'-nitrophenyl ether	88.9	76.9	55.4	62.7	71.0	85.6	66.6	80.0
10	2,3-Dichlorophenyl-4'-nitrophenyl ether	88.7	75.9	50.0	57.9	60.1	102	63.1	72.0
11	3,4-Dichlorophenyl-4'-nitrophenyl ether	86.6	75.7	50.6	61.0	51.8	84.1	64.9	84.3
12	2,4,6-Trichlorophenyl-4'-nitrophenyl ether	86.8	74.4	59.5	66.1	75.6	90.3	74.1	79.6
13	2,3,6-Trichlorophenyl-4'-nitrophenyl ether	86.3	76.5	66.0	71.5	91.0	107	70.9	72.6
14	2,3,5-Trichlorophenyl-4'-nitrophenyl ether	88.6	77.7	59.9	71.5	91.0	107	76.9	79.3
15	2,4,5-Trichlorophenyl-4'-nitrophenyl ether	85.1	72.9	52.4	60.8	62.2	85.2	63.8	70.7
16	2,4-Dibromophenyl-4'-nitrophenyl ether	86.1	70.7	57.1	56.3	69.8	82.1	58.1	68.4
17	3,4,5-Trichlorophenyl-4'-nitrophenyl ether	83.9	72.1	57.1	61.4	67.9	84.1	64.8	69.4
18	2,3,4-Trichlorophenyl-4'-nitrophenyl ether	83.6	72.2	43.3	55.0	73.5	77.2	57.6	68.3
19	2,4-Dichlorophenyl-3'-methyl-4'-nitrophenyl ether	85.6	72.2	57.1	34.1	63.1	65.8	44.3	55.8

[a] Experiments 1 and 2 were performed in parallel to determine losses during carbon dioxide depressurization. The extraction vessel was filled out with glass beads and the test compounds were spiked directly into the collection vials.

[b] Experiments 3 and 4 were identical samples (2.5 g sand spiked in an aluminum cup at 600 ng/g per compound) extracted in parallel at 250 atm/70°C/60 min dynamic.

[c] Experiments 5 and 6 were identical samples (2.5 g sand spiked at 600 ng/g per compound directly in the extraction vessel) extracted in parallel at 250 atm/70°C/60 min dynamic.

[d] Experiments 7 and 8 were identical samples (2.5 g sand spiked at 600 ng/g per compound) extracted in parallel at 150 atm/50°C/60 min dynamic.

TABLE 6. PERCENT RECOVERIES OF BASE/NEUTRAL/ACIDIC COMPOUNDS FROM SPIKED SAND EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE[a]

Compound no.	Compound	Supercritical carbon dioxide	Supercritical carbon dioxide with 200 µL acetone
1	Phenol	141	83.5
2	Bis(2-chloroethyl)ether	37.6	36.3
3	2-Chlorophenol	73.1	57.9
4	1,3-Dichlorobenzene	3.9	1.9
5	1,4-Dichlorobenzene	4.6	2.1
6	Benzyl alcohol	111	128
7	1,2-Dichlorobenzene	9.0	5.0
8	2-Methylphenol	111	129
9	Bis(2-chloroisopropyl)ether	45.1	42.8
10	4-Methylphenol	148	96.6
11	N-nitroso-di-n-propylamine	57.6	67.1
12	Hexachloroethane	5.7	0
13	Nitrobenzene	59.4	54.9
14	Isophorone	59.1	73.6
15	2-Nitrophenol	67.0	55.3
16	2,4-Dimethylphenol	93.3	71.7
17	Benzoic acid	0	0
18	Bis(2-chloroethoxy)methane	65.7	83.3
19	2,4-Dichlorophenol	104	75.7
20	1,2,4-Trichlorobenzene	42.9	36.7
21	Hexachlorobutadiene	36.9	29.6
22	4-Chloro-3-methylphenol	176	113
23	2-Methylnaphthalene	74.2	72.1
24	Hexachlorocyclopentadiene	67.9	63.3
25	2,4,6-Trichlorophenol	105	88.5
26	2,4,5-Trichlorophenol	121	96.1
27	2-Chloronaphthalene	81.1	82.0
28	Dimethylphthalate	49.0	71.1
29	2,4-Dinitrophenol	33.1	26.8
30	4-Nitrophenol	82.7	111
31	Dibenzofuran	89.1	92.3
32	2,4-Dinitrotoluene	71.9	87.5
33	2,6-Dinitrotoluene	87.8	85.0
34	Diethyl phthalate	48.5	72.5
35	4-Chlorophenyl-phenylether	83.6	90.1
36	4,6-Dinitro-2-methylphenol	49.6	53.3
37	4-Bromophenyl-phenylether	102	80.0
38	Hexachlorobenzene	113	79.9
39	Pentachlorophenol	66.4	58.2
40	Di-n-butylphthalate	51.9	77.8
41	Butylbenzylphthalate	32.1	63.3
42	Bis(2-ethylhexyl)phthalate	59.6	73.6
43	Di-n-octylphthalate	35.0	69.7

[a] The extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. Modifier (200 µL) was added to the matrix. The sample size was 9.3 g. The spiking levels were 21.5 µg/g per compound for the base/neutrals, and 18 µg/g per compound for the acidic compounds, except for 4-methylphenol, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and 4-nitrophenol which were spiked at 3.5 µg/g per compound.

TABLE 7. PERCENT RECOVERIES OF PAHs FROM SPIKED SAND AND SPIKED NIST STANDARD REFERENCE MATERIALS EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE

Compound no.	Compound	Sand[a] (9.3 g)	Sand with 200 µL acetone[b] (9.3 g)	Sand[b] (11.2 g)	Sand with 200 µL acetone[b] (11.2 g)	SRM-1649 Urban dust[c] (1 g)	SRM-1632a Coal[c] (1 g)	SRM-1633a Coal fly ash[c] (1 g)
1	Naphthalene	67.2	80.4	41.0	86.2	100	95.0	88.3
2	Acenaphthylene	81.7	78.4	62.7	92.9	95.3	92.8	88.8
3	Acenaphthene	87.8	81.2	65.9	88.7	104	93.0	89.5
4	Fluorene	86.7	80.2	68.6	89.1	101	94.6	89.2
5	Phenanthrene	85.7	79.0	63.0	91.8	118	95.0	87.5
6	Anthracene	84.6	77.5	64.4	88.1	93.8	91.7	85.7
7	Fluroanthene	85.7	78.4	64.2	87.6	88.8	92.6	90.7
8	Pyrene	89.3	82.7	69.5	89.9	70.0	94.8	87.4
9	Benzo(a)anthracene	85.8	82.1	77.0	88.8	14.5	96.7	88.6
10	Chrysene	76.8	82.6	66.3	89.2	26.7	96.7	88.6
11	Benzo(b)fluoranthene	97.0	83.5	70.2	88.5	20.0	104	88.1
12	Benzo(k)fluoranthene	63.7	84.1	62.9	88.6	30.0	98.9	100
13	Benzo(a)pyrene	70.4	81.7	67.2	92.3	19.2	100	92.7
14	Indeno(,2,3-c,d)pyrene	59.5	85.3	50.7	87.2	16.4	99.0	90.1
15	Dibenzo(a,h)anthracene	31.8	80.8	17.9	84.9	15.0	93.9	88.1
16	Benzo(g,h,i)perylene	24.3	79.9	16.6	87.0	12.8	93.8	85.2

[a] The extraction was performed at 150 atm/50°C/10 min static followed by 200 atm/60°C/10 min dynamic and then 250 atm/70°C/10 min dynamic. Single determination. Modifier (200 µL) was added to the spiked matrix (when applicable). The spiking level was 21.5 µg/g per compound.

[b] The extraction was performed at 150 atm/50°C/5 min static followed by 150 atm/50°C/55 min dynamic. Single determination. The spiking level was 21.5 µg/g per compound for the 9.3-g sample, and 17.9 µg/g per compound for the 11.2-g sample.

[c] The extraction was performed at 150 atm/50°C/5 min static followed by 150 atm/50°C/55 min dynamic. No compounds were collected from the second extraction that was performed at 200 atm/60°C/10 min dynamic followed by 250 atm/70°C/10 min dynamic. Single determination. The spiking level was 200 µg/g per compound.

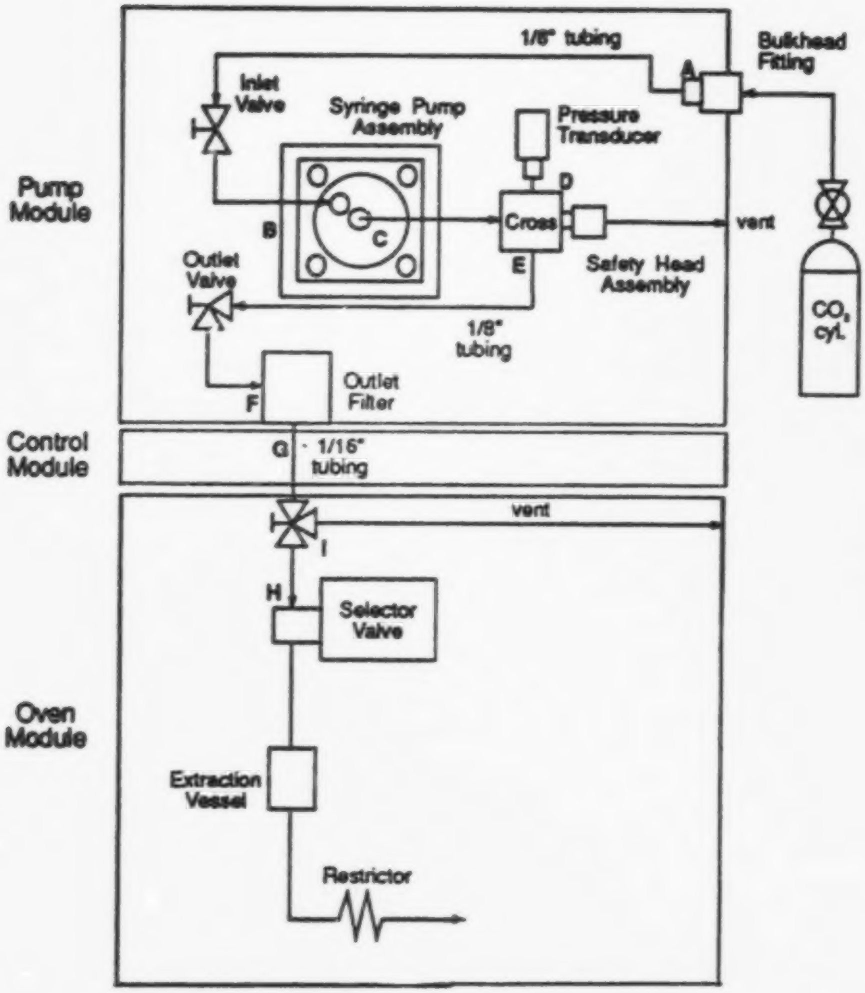

1/8" tubing
Bulkhead Fitting
A
Inlet Valve
Syringe Pump Assembly
Pressure Transducer
Pump Module
D
B
Cross
vent
C
E
Outlet Valve
Safety Head Assembly
CO2 cyl.
1/8" tubing
Outlet Filter
F
Control Module
G
1/16" tubing
vent
I
H
Selector Valve
Oven Module
Extraction Vessel
Restrictor

Figure 1. Schematic representation of SFE system

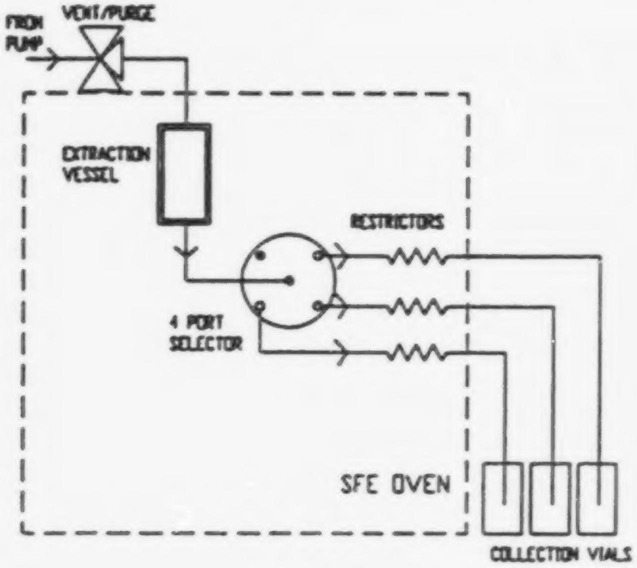

FROM PUMP
VENT/PURGE
EXTRACTION VESSEL
RESTRICTORS
4 PORT SELECTOR
SFE OVEN
COLLECTION VIALS

Figure 2. Schematic representation of extraction vessel, 4-port valve, restrictors, and collection vials